University of Alberta

Effect of solvent addition to oil sand processing

by

Sanjay Kumar Harjai ©

A thesis submitted to the Faculty of Graduate Studies and Research

in partial fulfillment of the requirements for the degree of Master of Science

in

Chemical Engineering

Department of Chemical and Materials Engineering

Edmonton, Alberta
Fall, 2007

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Your file Votre référence
ISBN: 978-0-494-33254-2
Our file Notre référence
ISBN: 978-0-494-33254-2

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ABSTRACT

In the present study, the impact of solvent (kerosene and naphtha) addition to oil sand ores on bitumen recovery and bitumen froth quality was investigated. Bitumen recovery tests for various oil sand ores were carried out using a Denver flotation cell at two operating temperatures of 25°C and 50°C. The addition of solvent (kerosene or naphtha) was carried out either by soaking the solvent in the ore prior to its processing or by spraying the solvent on the bitumen froth during flotation in the Denver cell.

It was found that when the extraction was carried out at 50°C, the solids-to-bitumen ratio in the produced bitumen froth was reduced with the addition of kerosene and bitumen recovery was improved with the addition of 2-4 ml of kerosene to 300 g of ore. Similar results were observed for naphtha addition at 50°C. At the extraction temperature of 25°C, the bitumen recovery was improved with the addition of kerosene, while the solids-to-bitumen ratio initially increased with the addition of kerosene and then decreased with more kerosene addition. The improvement in froth quality due to the solvent addition would be beneficial to the downstream bitumen froth treatment processes.

ACKNOWLEDGEMENTS

I would like to thank my supervisor Dr. Jacob Masliyah and co supervisor Dr. Zhenghe Xu, for their guidance and encouragement throughout the course of this thesis.

My gratitude extends to the Oil Sands group and the staff in the Department of Chemical and Materials Engineering at the University of Alberta specially for the support extended by Ms. Leanne Swekla, Ms. Shiau-Yin Wu and Mr. Jim Skwarok.

Special thanks to my parents for their blessings and encouragement, as well as to my son Nabhya Harjai, daughter Bhuvi Harjai and loving wife, Ashu Harjai for always being there for me.

Finally, I would like to thank the NSERC Industrial Research Chair in Oil sands Engineering for the funding that made this thesis project possible.

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NOMENCLATURE

AEUB	Alberta Energy and Utilities Board
BEU	Batch Extraction Unit
CSS	Cyclic Steam Stimulation
EUB	Alberta Energy and Utilities Board
FEP	Fluorinated Ethylene Propylene
GHG	Greenhouse Gases
HLB	Hydrophilic-Lipophilic Balance
LEE	Low Energy Extraction
LHES	Laboratory Hydrotransport Extraction System
MIBC	Methyl Iso Butyl Carbinol
NEB	National Energy Board
OSLO	Other Six Lease Operators
PPCO	Polypropylene COpolymer
PSV	Primary Separation Vessel
SAGD	Steam Assisted Gravity Drainage
SCO	Synthetic Crude Oil
THAI	Toe-to-Heel Air Injection
VAPEX	Vapour Extraction Process

1. INTRODUCTION

1.1. OIL SANDS OVERVIEW

Canada is ranked the second largest after Saudi Arabia in terms of global proven crude oil reserves (15% of world reserves). Most of these reserves are found in Alberta's oil sands. Oil sands are comprised of sand, heavy hydrocarbon, mineral rich clays and water, and are defined as a type of crude oil deposits that are substantially heavier (more viscous) than regular crude oils. The product obtained from the oil sands is bitumen that requires further upgrading to synthetic crude oil (SCO) or is diluted with lighter hydrocarbons to make it transportable by pipelines and usable by refineries. Alberta has large deposits of oil sands that underlie around 140,200 square kilometers (54,131square miles) of the northern part of the province. These deposits are mainly separated into three regions: Peace River, Athabasca (Fort McMurray area), and Cold Lake (north of Lloydminster). About 82% of the remaining established reserves are considered to be recoverable by in-situ methods and the rest is recoverable by surface mining methods. These oil sands deposits are estimated to contain approximately 1.7 trillion barrels of bitumen in-place, of which 174 billion barrels are proven reserves that can be recovered using current technologies. Total recoverable oil reserves are estimated at over 334 billion barrels. (Source: www.energy.gov.ab.ca)

The Alberta Energy and Utilities Board (AEUB) in its annual report, "Alberta's Reserves 2006 and Supply/Demand Outlook 2007-2016" details that the bitumen production surpassed conventional oil production by over 231% in 2006. Bitumen production from oil sands in 2006 was 458 million barrels averaging 1.25 million barrels per day (an increase of 18 % over 2005) as compared to conventional oil production of 198 million barrels averaging 543,700 barrels per day (a decrease of 5% from 2005). According to the AEUB, production averaged just over 1 million barrels per day (bpd) of bitumen in 2005 and is projected to increase to about 3 million barrels per day by 2015. At a projected production rate of 3 million barrels per day, the Athabasca oil sands reserves are estimated to last for over 400 years.

In mid-2006, the National Energy Board (NEB) of Canada estimated the operating cost of a new mining operation in the Athabasca oil sands to be $9 to $12 per barrel, while the cost of an in-situ SAGD operation (using dual horizontal wells) to be $10 to $14 per barrel. This operating cost of oil from oil sand is very high as compared to the operating cost for conventional oil wells which range from less than $1 per barrel in Iraq and Saudi Arabia to $6 and up in the United States and Canada. In addition to the high operating cost, the capital cost of the equipment used in oil sand mining, such as the huge shovels required to mine the oil sands and the dump trucks used to haul the mined oil sands to processing site make capital costs a major consideration in starting the production of bitumen from oil sands. The NEB estimates that the capital costs raise the total cost of production to $18 to $20 per barrel for a new mining operation and $18 to $22 per barrel for a SAGD operation. This does not include the cost of upgrading bitumen to synthetic crude oil, which increases the final cost to $36 to $40 per barrel for a new mining operation.

However, the economics of oil sands have improved dramatically due to the conventional crude oil price increase during 2004-2006. At a world price of $50 per barrel for a crude oil, the NEB estimates an integrated mining operation would make a rate return of 16 to 23 percent, while a SAGD operation would return 16 to 27 percent. Prices in 2006 have been considerably higher than $50 per barrel, even hovering around $70 per barrel for certain periods in the duration. As a result, the capital expenditures in the oil sands announced for the period 2006 to 2015 exceed $100 billion, which are twice the amount projected in 2004. Although high crude oil prices make the cost of production of bitumen from oil sands very attractive, sudden drops in crude oil price would leave oil sand operators unable to recover their enormous capital costs. However, the development of commercial production is made easier by the fact that exploration costs are virtually negligible. The exploration cost is a major factor when assessing the economics of drilling in oil fields for conventional crude oil. The locations of the oil deposits in the oil sands are well known and an estimate of recovery costs can usually be made easily. The developments as well as the improvements in the bitumen mining, extraction and upgrading processes have been made by the extensive research work done at the commercial scale by the industry and at the laboratory scale by various Research Centres and Universities across Canada and around the World. These research efforts have contributed to continous improvement in process technologies leading to the increase in profit margins of oil sand operations.

1.2. BITUMEN EXTRACTION FROM OIL SANDS

G.C. Hoffman (1883) of the Geological Survey of Canada was one of the pioneers who first attempted the separation of bitumen from oil sand with the use of water. Sidney Ells (1915) of the federal mines branch began to study oil sands separation techniques and used the bitumen to pave 600 feet of roads in Edmonton, AB that lasted for 50 years. Dr. Karl Clark (1928) of the Alberta Research Council was granted a patent for the hot water extraction process, which is still the basis of the current commercial extraction processes used in oil sand extraction plants. (Source: "History: Oil Sand Discovery Center fact sheet").

The first large scale commercially successful application of Clark Hot Water Extraction Process (CHWE) was accomplished in 1967 by the Great Canadian oil sands (GCOS) now called Suncor Energy Inc. In the late 1970's Syncrude Canada Limited started their commercial oil sand operations in Fort McMurray area. This was followed by commencement of oil sands extraction operations by Albian Sands Energy Inc. in early 2003. Since then, dozens of projects have been announced for bitumen extraction from oil sands across various locations around Fort McMurray and Edmonton (either integrated along with up-grading units or on a stand-alone basis). The basic process of bitumen extraction from oil sands consists mainly of following process units/ sections:

- **Oil sand mining:** Removal of over burden followed by oil sand mining using shovels which have a capacity of the order of 100 MT. The mined oil sands are transported to the preparation unit using trucks having capacities as high as 400 MT. Typical oil sand ore consists of around 8-14% bitumen and the rest is solids and water.
- **Ore preparation:** The mined ore is crushed and mixed with water to make oil sand slurry using rotary breakers, cyclo-feeders, mixing boxes and screens etc. These types of equipment aid in mixing the oil sand lumps and in aerating the formed slurry. The slurry thus formed is transported to the next process step-using pipeline called hydrotransport pipeline.

- **Bitumen extraction unit:** The aerated slurry is received in huge vessels called Primary Separation Vessels (PSV), which separates the slurry into bitumen froth, middling, and tailings. At the feed inlet, the slurry is diluted with the addition of more water. For an average ore, the feed to PSV contains around 7% aerated bitumen, 43% water and 50% solids by weight. After around 20-40 minutes of settling, the floated bitumen is separated as primary froth, which on average contains 60% bitumen, 30% water and 10% fine solids, by weight. The coarse sand settles to the bottom of the separation vessel and is removed as a tailings stream. The middle stream from the vessel called middlings is processed in flotation cells to recover the fine oil droplets that cannot float to the top of the vessel.
- **Froth treatment unit:** The aerated bitumen from PSV and the flotation cells is de-aerated using steam and is further cleaned. Diluents such as naphtha (Naphthanic treatment) or hexane (Paraffinic treatment) are used to reduce the density of froth to further separate solids and water from the bitumen froth. The bitumen quality after naphthanic froth treatment is 1.5-2.5% water (0-100 ppm for paraffinic treatment) and 0.4-0.8 % solids (500-800 ppm for paraffinic treatment).
- **Tailings Disposal:** The tailings from the separation vessel and flotation cells combine to form the final tailings slurry which is pumped to large tailings ponds for treatment and settling
- **Upgrading:** The cleaned bitumen after froth treatment is upgraded into synthetic crude oil for refining into useful petroleum products. Typical configuration includes diluent recovery unit (DRU), coker / hydrotreaters etc.

A generic flow diagram of oil sand mining to bitumen upgrading is shown below in figure 1.1

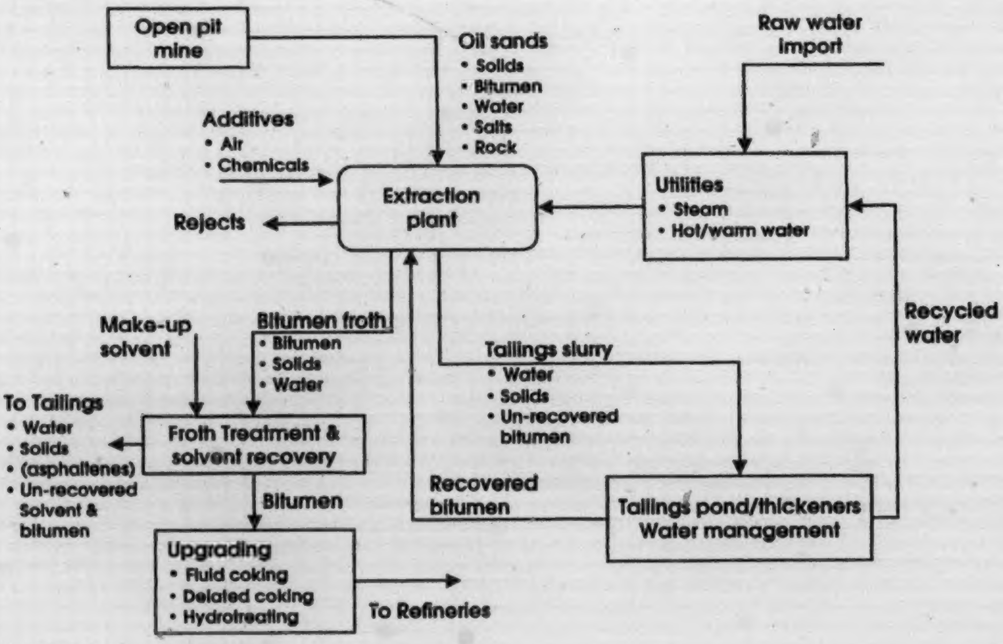

Open pit mine
Oil sands
• Solids
• Bitumen
• Water
• Salts
• Rock
Raw water import
Additives
• Air
• Chemicals
Extraction plant
Rejects
Utilities
• Steam
• Hot/warm water
Make-up solvent
Bitumen froth
• Bitumen
• Solids
• Water
Recycled water
Tailings slurry
• Water
• Solids
• Un-recovered bitumen
To Tailings
• Water
• Solids
• (asphaltenes)
• Un-recovered Solvent & bitumen
Froth Treatment & solvent recovery
Bitumen
Recovered bitumen
Tailings pond/thickeners Water management
Upgrading
• Fluid coking
• Delated coking
• Hydrotreating
To Refineries

Figure 1.1: Generalized scheme for oil sands processing using water-based extraction processes (Masliyah et al. 2004)

Another approach to bitumen extraction from oil sands is in-situ production in which bitumen is separated from the sand while the oil sands deposit is still in place underground. The simplest method is primary or "cold" production, which is employed in the reservoirs where the oil can flow to the surface via wells without the introduction of heat. Many in-situ operations require the addition of heat to make the bitumen less viscous so that it can be pumped up to the surface. Some in-situ operations use cyclic steam stimulation (CSS) process, in which steam is added to the oil sands via vertical wells to separate bitumen, which is subsequently pumped to the surface using the same well. Other in-situ operations use variations of the steam assisted gravity drainage

(SAGD) process. This process consists of adding steam to the oil sands using a horizontal well and simultaneously lifting the bitumen using another horizontal well located just below the steam injection well. Other emerging approaches to in-situ production include the vapor recovery extraction method (VAPEX), which involves the use of solvents as a supplement or alternative to steam and underground combustion method (THAI Process). Typically, about two tons of mined oil sand ore yields about one barrel (159 liters) of synthetic crude oil. Both mining and in-situ operations use large volumes of water for extracting bitumen from the oil sands. Between 2 to 4.5 barrels of water is withdrawn from the river to produce each barrel of synthetic crude oil (SCO) in a mining operation. In SAGD operations, although 90 to 95 percent of the water used for steam to recover bitumen is reused, every cubic meter of bitumen produced still requires about 0.2 cubic meters of additional groundwater. Some surface water is used but most operations use fresh and saline groundwater. (Source: "Oil Sand Discovery Center fact sheet").

1.3. OBJECTIVE OF THESIS

The objective of this study is to analyze the impact of addition of industrially viable solvents like kerosene and naphtha to the oil sand ores on bitumen recovery and solids to bitumen ratio in the bitumen froth generated. The experimental work uses Denver Flotation Cell for generating bitumen froth from poor processing ores, good processing ore and weathered ores with solvent addition at 50°C and 25°C. The froth is analyzed using Syncrude Dean Stark method. The addition of a solvent (typically using 2 ml to 15 ml on 300 g of oil sand ore) has been carried out either by soaking the solvent in the ore before processing it or by spraying the solvent on the bitumen froth during the froth generation process in the Denver cell. More specific objectives of the study on account of addition of solvent are given below:

- To investigate the improvement / variation of bitumen recovery at 50°C and 25°C extraction of bitumen froth from different types of oil sand ores.
- To investigate the reduction / variation in solids and solids to bitumen ratio in the froth generated from different types of ores.
- To analyze the particle size distribution of solids in the bitumen froth generated for different types of ores.
- To analyze the improvement / changes in the morphology of bitumen froth generated from poor processing ore and weathered ores using solvent at 25°C as compared to the morphology of good processing ores both at 50°C and 25°C.
- To analyze the variation in the physical properties of solids recovered in the bitumen froth and tailings water.
- To analyze the solvent (kerosene) loss in the tailings water during extraction process of kerosene soaked oil sand ore.

1.4. OVERVIEW OF THESIS

This thesis is organized in the following way:

- **CHAPTER 1** is an introduction and overview of the oil sands of western Alberta followed by the objective and organization of the thesis.
- **CHAPTER 2** includes a literature review of the previous studies on the fundamentals of oil sands, factors affecting mechanism of bitumen recovery from oil sands, the laboratory procedures developed and used to understand the nuances of bitumen extraction. This is followed by a review of the relevant work on the

impact of using solvents and additives on bitumen extraction as well as bitumen froth morphology.

- **CHAPTER 3** includes the preliminary tests carried out to observe the impact of solvent addition on reduction of solids or solids to bitumen ratio in bitumen froth generated from different types of ores. Experiments are based on simple jar tests using bitumen froth and solvents like naphtha and kerosene or addition of solvent on the nascent bitumen froth during the froth generation in the Denver Flotation Cell.
- **CHAPTER 4** includes the observations and results obtained for bitumen recovery as well as solids to bitumen ratio for different types of ores, where solvent were soaked in the ore before bitumen extraction was carried out at 50°C and 25°C. This is followed by the morphology analysis using Confocal Laser Scanning Microscopy (CLMS) for the bitumen froth obtained from kerosene soaked ores at 50°C and 25°C extraction.
- **CHAPTER 5** summarizes the results and states the conclusions of the study.
- **CHAPTER 6** identifies areas that require further research.

2. LITERATURE REVIEW

2.1. OIL SANDS COMPOSITION AND CHARACTERISTICS

Oil sand is often referred to as "tar sand," because the bitumen (or oil) contained in it resembles the black, sticky tar. However, the term "tar sand" is incorrect. Tar is a manufactured heavy end product produced through the distillation of crude oil. The heavy thick oil, which is part of oil sand, is BITUMEN and not tar. These oil sands primarily constitute bitumen, water, sand and clays. The bitumen content in oil sand deposits varies from 6% - 18%. Oil sand ores with more than 12% bitumen content are considered rich grade and those with less than 8% are considered very poor grade. The poor grade ores are usually not considered economically feasible to mine, although these are mined and processed with a blended stock of higher-grade oil sand. Typically the total content of bitumen and its connate water is fairly constant at around 16% with solids content constituting the remaining 84% of the oil sands. (Source: “Oil Sand Discovery Center fact sheet”).

Oil sands of northern Alberta are best defined as "hydrophilic" or "water wet." Each grain of sand is covered with a thin film of water, which is then surrounded by a mass of heavy oil bitumen. The electrostatic forces arising from the electrical double layer at the oil/water and water/sand grain interfaces are assumed to be responsible for stabilizing the water film around the sand grains (Takamura, 1982; Hall et al., 1983; Anderson, 1986). The thickness of the assumed thin water film sandwiched between a sand grain and bitumen is estimated to be about 10 nm (Takamura, 1982; Hall et al., 1983). The reason for the easy processability of oil sands of Athabasca has been attributed to this hydrophilic characteristic of the sand grains as compared to the hydrophobic character of sand grains of Utah oil sands in USA (Sepulveda and Miller, 1978; Miller and Misra, 1982). The oil sands of Athabasca are bonded firmly together by grain-to-grain contact and the viscosity of bitumen in these oil sands is relatively low. During winter, the water layer in the oil sand freezes which makes oil sands as hard as cured concrete and difficult to mine. During summer, it is as soft as molasses that makes driving conditions for mining trucks in the oil sand mining area treacherous.

It has been established that oil sand is a complex mixture of sand, clay fines, connate water and bitumen (Bowman, 1967). The level of fines and clays play a major role in bitumen flotation and separation. Therefore, knowledge of the solid particle size distribution of an ore body is one of the important parameters in oil sand ore characterization. Typical composition of solids in oil sand comprises of 92% quartz with traces of mica, rutile, zircon, tourmaline, and pyrite (Carrigy and Kramers, 1973; Boon, 1978). Quartz is the most abundant component where-as clay is the only component that constitutes fines. In oil sands terminology, fines are defined as mineral solids, which are smaller than 44 microns. Kaolinite and illite clays with trace amount of montmorillonite is the main constituent of clay fines in the ore. It is observed that a high-grade oil sand contains less fines; where as poor-grade oil sand contains high amounts of fines (Masliyah, 2000).

The efficiency of bitumen flotation and recovery depends on the nature of bitumen; fine solid and clay content, salts concentration and its type in the connate water in oil sands. The separation efficiency and kinetics also depend on the temperature of the slurry, which impacts the viscosity and density of the bitumen in the slurry. The surface properties like wettability (contact angle), surface tension, interfacial tension and electric potentials of sand and bitumen also affect the separation efficiency of bitumen from oil sand ores (Masliyah, 2000).

2.2. FACTORS AFFECTING BITUMEN RECOVERY

It has been recognized that three sub-processes are responsible for controlling the bitumen recovery from oil sands: (i) bitumen recession from sand grain, (ii) bitumen attachment to an air bubble, and (iii) flotation of aerated bitumen in a separation vessel (Masliyah and Gray, 2003). Extensive study has been carried out in the last few decades to understand the factors affecting the bitumen recovery from oil sands. Masliyah et al. (2004) has given details of the conceptual stages for bitumen liberation and aeration in extensive details that describe ablation of an oil sand lump, formation of three phase contact point, bitumen recession onto itself over a sand grain surface followed by bitumen disengagement from a sand grain and other details involved in the mechanism of bitumen recovery from oil sands. Any process or process aid that can enhance the efficiency of any of these steps would lead to the improvement of bitumen recovery using water based extraction processes.

Clark (1929) ascribed the thin layer of water around a sand particle as the driving force for displacing the bitumen from the sand. Research council workers thought that the deterioration of bitumen recovery from oil sands was due to the loss of natural water content in the oil sand matrix or disappearance of the water film separating the oil from the sand surface leading to direct attachment of oil with the sand.

Ali (1975) studied the poor processability of weathered ores and attributed the loss of connate water by evaporation as the reason for the poor processing. However, he ascribed that the destruction of the structures of the oil sands was responsible for the detrimental effect of indigenous water loss leading to direct oil-solid contact and hence the poor processability of weathered ores.

Dai and Chung (1995) studied the mechanism of bitumen recovery using hot water process. Their investigation shows that the bitumen can be easily separated from sand matrix at pH>6 and the separation becomes difficult at pH<6. They advocated that although bitumen can be totally liberated from sand grains without adding process aids, addition of sodium hydroxide improves the bitumen recovery.

Shuyuan et al. (1995) studied the effects of several factors on bitumen recovery by hot water as well as the pyrolysis for Chinese tar sands. They concluded that hot water extraction was not equally effective for all types of ores. Therefore, the type of tar sand plays a significant role in choosing an appropriate process for higher degree of bitumen recovery.

Basu et al. (1996, 1997) advocated a modified mechanism of bitumen liberation from oil sands by using alkali hot water extraction method where the concept of a pH cycle was considered instead of operating the process at constant value of a pH=8.2. It was observed that a pH cycle from low to a high value would yield faster film thinning, film rapture and bitumen displacement.

Khraisha (1997) studied the kinetics of solvent extraction of tar sand and showed that the extraction process was governed by the diffusion of soluble material according to thin film theory. The kinetic parameters of pyrolysis have been determined based on "first-order rate expression and their values were found to be in agreement with other published data in the literature.

Liu et al. (2004) studied the effect of water loss due to weathering of the ore by artificially weathering the oil sand ore at laboratory scale. They treated the ore in an oven at 50°C under controlled environment and observed that water loss contributed to more than 90% of the total weight loss of oil sand ore as a result of artificial weathering process. They observed that direct contact between bitumen and sand grains along with the high concentrations of divalent ions in the connate water makes the surface of sand grain more hydrophobic due to transfer of surfactants from the bulk bitumen to the solid surface and leads to poor recovery.

Commercial operations using water based extraction process face a challenge of reduced bitumen recovery for high fines ores or weathered oil sand ores (sometimes called oxidized ores). For such ores, small dosage of sodium hydroxide in traditional Clark Hot Water Extraction is not a sufficient process for desired recovery of bitumen. Wallwork et al. (2003) found that bitumen recovery from a weathered ore containing 11.5% bitumen by weight was less than 20% in contrast to a more than 90% bitumen recovery for good processing ores with similar feed bitumen content. The reason for poor bitumen recovery from weathered ore was attributed mainly to the deteriorated bitumen-air bubble attachment.

2.3. LABORATORY PROCEDURES FOR BITUMEN EXTRACTION

The impact of operating parameters and additives has always been an area of interest and a basis for improving the bitumen recovery from oil sands. A number of techniques for testing of oil sand processability have been developed over last few decades. Clark and Blair (1923) introduced the first hot water bitumen extraction laboratory scale plant at University of Alberta. Bichard (1987) used a jar test to conduct research on oil sands processability. Flotation has found extensive use in bitumen extraction from oil sands (Sanford and Seyer, 1979; Hepler and Hsi, 1989; Hepler and Smith, 1994; Kasongo et al., 2000; Zhou et al., 2004). It has been established that water based extraction processes work better in an alkaline aqueous medium (Clark and Pasternack, 1932; Sanford, 1983; Bichard, 1987; Liu et al. 2004, 2005)

Sanford and Seyer (1979) introduced a laboratory scale hot water separation unit for extracting bitumen from Athabasca oil sands. The Batch Extraction Unit (BEU) developed by them was an extension of similar earlier units but it consumed a smaller size of sample of homogenized oil sand for studying the oil sand processability. The BEU unit was extensively used to study the impact of changes in process operating parameters and addition of chemicals on the hot water extraction process at constant process operating parameters. One of the major studies carried out using NaOH indicated that NaOH addition during hot water extraction leads to neutralization of organic acids in the bitumen, leading to release of surfactants from bitumen in the oil sand ores. These released surfactants from bitumen play an active role during bitumen extraction and act as primary agents responsible for improvement in the bitumen recovery. In continuation to the study carried out using NaOH, Sanford (1983) advocated that over dosage of NaOH might prove detrimental and there exists an optimum quantity corresponding to maximum bitumen recovery. The BEU offers a good means to screen out various process variables, but it should be noted that the operating conditions for the BEU are set for an 80°C oil sand digestion similar for a tumbler. New BEU operating conditions are to be devised for a low temperature processing conditions.

Wallwork (2003) developed a Laboratory Hydrotansport Extraction System (LHES) at University of Alberta to test ore processability for several oil sands operators. The main part of the unit is a 3-meter glass pipe loop having a 17 mm inner diameter. The unit incorporates a visualization tube inside the froth collection vessel. The tube allows aerated bitumen droplets to be observed and recorded through a CCD video camera. A second CCD camera analyzes bitumen separation from the sand grains. Bitumen recovery is measured by collecting the bitumen froth in the froth collection vessel. This laboratory scale equipment has been used so far to analyze the effect of air addition, temperature variation and ore type on its processability and bitumen recovery.

Luthra et al. (2004) developed an alternative method for estimating bitumen recovery using visualization tools to observe oil sand slurry undergoing digestion. A Couette flow device has been used at bench scale level that uses small amounts of oil sand and water. In this technique, an oil sand sample together with water and additives are placed in a gap of two concentric cylinders with the inner cylinder rotating. Air is bubbled through the oil sand slurry, while it is subjected to controlled chemical conditions and shear environment. During this process, images of the slurry are captured and analyzed using image analysis software. The analysis of the image is based on the fraction of black areas set by predetermined gray scale intensities. The variation of the black area with time is used as a measure of bitumen liberation and recovery. This technique is useful in quick estimates of final recovery and can also be used for studying the kinetics of the liberation and recovery processes. The experimental set-up offers great flexibility in selecting conditions for the digestion of oil sands.

Friesen et al. (2004) developed a technique in which a microscope and video cameras are used to observe slurry stirred in a glass cell to evaluate, on a comparative basis, the effect of conditioning parameters on the bitumen recovery. Several ores and their blends were studied and found to exhibit large differences in their conditioning behavior. The method offers the capability of diagnosing ore processability problems and optimizing slurry conditioning. The technique proved useful in analyzing the factors responsible for efficient extraction of bitumen from oil sand ores and concluded that proper conditioning of oil sand/water slurry depends on such variables as ore grade, temperature, mixing intensity and duration as well as water chemistry.

Zhou et al. (2004) used a laboratory Denver flotation cell to assess bitumen recovery from the Athabasca oil sands. In their study, a methodology was developed to evaluate the effect of operating parameters on the processability of oil sands using a Denver cell. A new concept of "true flotation recovery" has been advocated to describe the bitumen recovery as a result of bitumen-bubble attachment during the extraction process by subtracting bitumen recovered in the froth by entrainment with water. The experimental results indicated that "true flotation recovery" is a more sensitive and meaningful marker than overall bitumen recovery to evaluate the processability of oil sands using small-scale laboratory test units.

2.4. IMPACT OF SOLVENTS ADDITION ON BITUMEN VISCOSITY

Viscosity is a measure of the resistance of a fluid to its deformation under stress. It describes internal resistance of fluids to flow and may be thought of as a measure of fluid friction. Bitumen behaves as a Newtonian fluid for a given temperature and pressure. Various investigations have led to the conclusion that there is a close correspondence between bitumen recovery and bitumen viscosity (Schramm et al. 2003) and bitumen viscosity is indeed an important property to consider in oil sand processing (Drelich et al. 2006). In the Utah oil sands processing, kerosene is added to the slurry to reduce the bitumen viscosity to < 1.5 Pa.s in order to make it processible at digestion temperature of 50-60°C (Drelich et al. 1995).

Seyer and Gyte (1989) have compiled data on the impact of temperature variation and solvents addition on viscosity for Athabasca and Cold Lake bitumen. The results of adding of alkane solvents at 25°C to Athabasca bitumen and solvents such as methylene chloride, toluene at 38°C for Cold Lake bitumen indicated promising results of reduction in bitumen viscosity. Naphtha addition of 20-30% (w/w) to bitumen has been shown to reduce the viscosity from 10^6mPa.s to 10^3-10^2mPa.s.

Hupka et al. (2004) studied the impact of kerosene addition on the viscosity of bitumen at 50°C and 90°C from various oil sand sources in USA as well as one from Athabasca. The bitumen phase viscosity as a function of kerosene content in the bitumen-kerosene blend is presented in Figure 2.1. They concluded that the amount of kerosene to be added to a given oil sand depends on the viscosity of original bitumen, oil sand grade and temperature of processing. The estimation of addition levels can be predicted by using the bitumen viscosity curves developed as a part of the study. The study showed that to achieve a satisfactory coefficient of separation, the bitumen viscosity must be reduced to below 2 Pa.s at the processing temperature for a predetermined conditioning time (termed as penetration time necessary for the diluent to mix with oil sand prior to digestion in order to uniformly reduce bitumen viscosity).

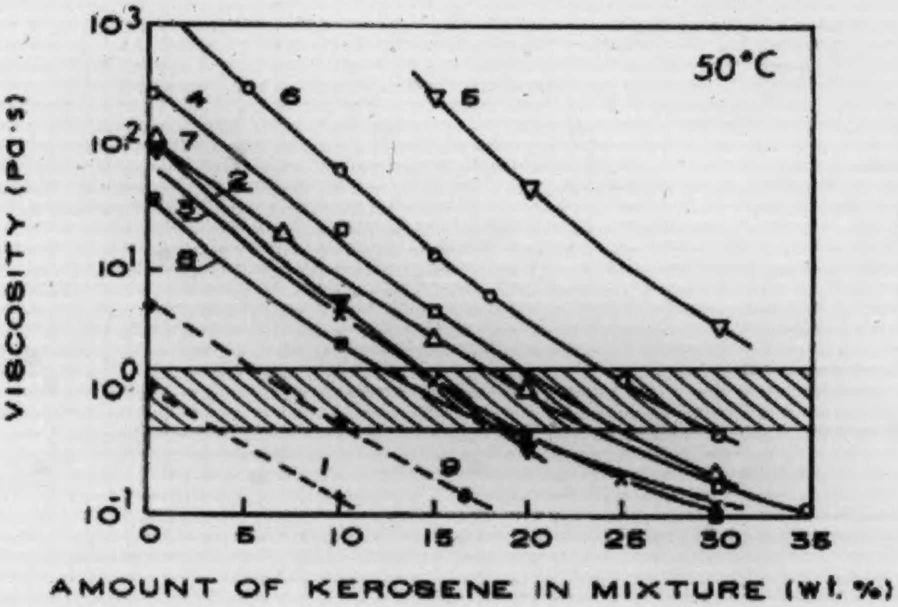


Figure 2.1: Plasticizing effectiveness of kerosene for bitumen from different oil sand deposit at 50°C. 1. McKittrick, 2. M. West II, 3. Asphalt Ridge, 4. P.R Spring Rainbow, 5. P.R. Spring South, 6. Sunnyside, 7.Whiterocks, 8. Wyoming I, 9. Athabasca. (Hupka et al 2004)

Mehrotra (1991, 1992)$^{(1)}$, Puttagunta et al. (1992)$^{(2)}$ and Mehrotra et al. (1996)$^{(3)}$ carried out extensive work and developed correlations for viscosity prediction of hydrocarbons and more specifically for bitumen. These correlations provide the means of predicting viscosity of bitumen diluted with liquid hydrocarbons and / or diluents (solvents) over a wide range of conditions (Masliyah 2000).

Moran et al. (2004) measured the bitumen viscosity at room temperature using a drop shape recovery technique, which has been defined to be immune to the problem of dissipative heating. The method used in this technique involves stretching a small droplet of bitumen (as small as several micrometers) with micropipettes and allowing it to recover to its original spherical shape. The shape recovery technique is caused by capillary forces and rate-limited by the droplet viscosity. The droplet viscosity can be determined accurately from the relaxation dynamics using interfacial tension values. In this shape recovery experiments, dissipative heating is independent of the shear rate and varies inversely with the viscosity as observed in the conventional viscometers where the problem of dissipative heating often increases linearly with the viscosity and quadratically with the shear rate.

2.5. IMPACT OF ADDITIVES OR SOLVENTS ADDITION ON IMPROVING BITUMEN RECOVERY

Recent developments in the experimental and analytical techniques in oil sands research have made it possible to examine the role of the operating parameters in each individual sub-process of bitumen extraction. The results of research carried out to date and commercial operations of oil sands extraction practice for poor-processing ores indicated that apart from adjusting the physical parameters, such as temperature, aeration, mechanical agitation, etc., (Masliyah et al. 2004), certain types of dispersing agents such as caustic, silicates, and phosphates (Bichard et al. 1987) are required to improve bitumen recovery from poor-processing oil sand ores. Silicates have been used as chemical additives to improve the bitumen recovery since early days of oil sands extraction research in the context of the hot water extraction process during 1920-30s (Clark et al. 1985). Caustic has been used in the commercial operation due to its low cost and easy availability for improving the bitumen recovery. Inorganic dispersants have been tested in a number of research experiments to check the effectiveness of these additives in enhancing bitumen recovery, (Sanford et al., 1979). However no clear conclusions have been drawn so far upon the category of chemicals that would perform consistently.

The advancement and expansion of oil sands exploration in the last couple of years in Northern Alberta have led to increased need of emphasis on low energy extraction processes, i.e., using warm water (50°C) or cold water (25°C). The underlying objective of this need is to reduce energy consumption while maintaining bitumen recovery efficiency similar to the conventional Clark Hot Water Extraction (CHWE) process operating at 80°C. The development of the Other Six Lease Owners (OSLO) cold-water process and Syncrude Low Energy Extraction (LEE) process (Logan et al. 1994; Kasperski, 2001) are major steps towards this direction. These processes are based upon usage of process aids, such as kerosene and methyl isobutyl carbinol (MIBC) to improve bitumen recovery at low temperature from oil sand ores. The OSLO extraction process is a non-caustic method used for operating temperatures of 30^oC-90^oC that uses collector (kerosene) and frother (MIBC) in a 2:1 ratio to improve bitumen recovery. The LEE process is carried out between 5^oC and 35^oC, and uses MIBC and kerosene in a 1:2 mix. The amount of MIBC and kerosene varies depending on the ore grade. Low-grade oil sands need more MIBC / kerosene to attain desired levels of bitumen recovery (Kasperski, 2001)

Clark and Pasternack (1932, 1944) studied the impact of alkaline additives on bitumen recovery. They concluded that addition of sufficient amount of alkaline additives in the presence of surface-active agents led to considerable increase in bitumen recovery. However they observed that bitumen recovery is adversely affected by the presence of certain type of clays in the oil sands.

Hupka et al. (1983); Hupka and Miller (1991) used kerosene to reduce bitumen viscosity during pretreatment step while investigating the effect of bitumen viscosity on bitumen recovery using hot water process. Lab experiments showed that pretreatment of oil sand with kerosene (10 wt. % kerosene) or the use of MIBC / kerosene was beneficial for bitumen liberation and hence bitumen recovery (Basu et al. 1997, 1998; Drelich and Miller, 1993).

Sury (1990) received a U.S patent for low temperature bitumen recovery process. He propounded a low temperature process for extracting bitumen from oilsands. The process comprises of mixing the oil sand slurry with a conditioning and/or frothing agent for a period of time sufficient to release bitumen from oil sands at a temperature in the range of about freezing temperature to 35°C, preferably in the range of 2°C to 15°C. The conditioning agent advocated, is a flotation agent having the characteristics of kerosene, diesel or kerosene/diesel together with a frother having the characteristics of methyl-isobutyl-carbinol (MIBC). Conditioning agent like kerosene was added in the range of 100-800 ppm and frothing agent like (MIBC) was added in the range of 50-400 ppm to improve the bitumen recovery by low temperature extraction.

Drelich et al. (1996) studied bitumen spreading and formation of thin bitumen film at an air water interface for bitumen diluted with kerosene. Samples of the unconsolidated Whiterocks oil sand (7.6 wt. % bitumen) were treated with 10 wt.% kerosene (kerosene addition based on the bitumen content in the ore). The samples were submerged in alkaline solutions in a glass cell and the changes in the sample characteristics, especially bitumen spreading on gas bubble surfaces was observed through a stereoscopic microscope. It was concluded that due to the presence of kerosene in the bitumen, a balance of interfacial tension in the system favored spreading of the bitumen over the entire gas bubble rather than forming bitumen lenses. Positive spreading coefficient led to the spreading of bitumen over the air bubble surface. The spreading coefficient reached a value close to zero when the system approached the equilibrium state. Microscopic investigations indicated that initial spreading of bitumen film precursor assisted the bitumen film spreading because the bitumen film precurser reduced the surface tension of the aqueous phase. It was deduced that due to the presence of kerosene, spreading of bitumen over the air bubble at the low temperature was fast, in contrast to other studies which showed extremely slow spreading of bitumen over the air bubble surface below 50°C operation. According to the microscopic observations it was concluded that the kinetics of spreading depends on the physical properties of bitumen, i.e., viscosity and density.

Schramm et al. (1998) studied the beneficial impact of addition of chemical additives, including polar organic solvents like toluene, xylene, heptane, MEK, MIBK and 2-propanol. These additives were added during the processing of oil sand ore mainly as under-wash or spray-wash treatment of froth during flotation. The experiments were carried out using a standard batch extraction unit (BEU). The chemical additions to the nascent froth were achieved either by addition of a slug of an additive before or at a fixed time during the froth formation step, or continuous addition from above on the froth throughout the froth formation process. Most of these experiments were conducted at 82°C with few at 50°C using nitrogen as the flotation gas in most of the experiments. It was observed that a small chemical addition during the nascent froth process lead to higher quality froth without sacrificing bitumen recovery or increasing tight emulsion-forming tendency. The improvement in the froth quality, in turn, led to a substantial increase in the throughput of froth handling and treatment plants. For example the results obtained by the addition of 2-propanol for the froth quality improvement measured in this work translate into a 16% volume reduction, on a unit volume of bitumen-treated basis, which represents a substantial increase in froth handling and treatment plant throughput.

Khraisha (1999) investigated the extraction and pyrolysis of tar sand from Wadi Isal, Jordan. The bitumen from tar sand samples was extracted using different technique called the Arm-field solid liquid extraction unit (UOP4). The results of investigation showed that the hot water extraction technique was ineffective for these tar sand because only a small amount of bitumen was obtained even at 80°C. Important parameters like solvent type, mixing time, operating temperature, particle size and alkali concentration was identified to be critical for bitumen recovery. Solvent addition proved to be one of the more important process parameters. In this work, kerosene was tested as a solvent because hot water extraction on its own without solvent resulted into very low bitumen recovery. The extraction using kerosene as a solvent gave a bitumen recovery upto seven times more than that obtained by hot water alone under the same operating conditions without NaOH addition. The higher contents of resins, asphaltenes and oxygen in the tar have been considered to be the reason behind low bitumen recovery by hot water (Shuyuan et al., 1995).

Schramm et al. (2001) investigated the impact of the addition of demulsifiers, mostly water-in-oil (W/O) emulsion breaking agents on the nascent froth. The addition of these demulsifiers was found to result in coalescence of water droplets and have improvement in the separation efficiency of these water droplets from the nascent froth. It was observed that certain combinations of surfactants and solvents when added in small amounts during the nascent froth generation process caused significant reductions in froth water content without sacrificing bitumen recovery. Addition of low to medium HLB surfactants such as Span 80 (HLB 4.3) and Tween 85 (HLB 11) had no significant effect beyond the influence of the carrier solvent (e.g., 2-propanol) but the addition of high HLB surfactants, such as Tween 80 (HLB 15) or Alcopol O (HLB 20) led to a significant reduction in water content. This has been found to be in agreement with the use of high HLB surfactants to destabilize water-in-oil emulsions. The results of the investigation suggest that for nascent froth treatment one needs surfactants of higher HLB values (ca. 15–20) than are typically required for marine oil spill emulsion treatments (ca. 8–12). Some of the froth quality improvement determined could represent a significant increase in froth handling and treatment plant throughput. For example, the water content reductions of about 10% observed in some cases would lead to a volume reduction of about 15% on a unit volume on bitumen-treated basis in commercial practice.

Liu et al. (2002) introduced a novel concept of using reactive oily bubbles as a carrier in flotation. In addition to the role of agglomerating fine particles, the surface properties of air bubbles coated with a thin layer of oil film could be controlled in a better manner. The results demonstrated a much higher contact angle and stronger collecting power by reactive oily bubbles. Additionally, the undesired side effects of adding collectors directly in the aqueous phase were observed to be greatly reduced. Selective flotation by using reactive oily bubbles was demonstrated only in single mineral flotation systems with a modified micro-flotation cell .

Wallwork et al. (2003) studied the extraction performance of poor processing oil sand ores using air-kerosene bubbles in a novel laboratory scale pipeline loop. It was observed that the use of oily bubbles generated with the addition of kerosene to air substantially enhanced bitumen recovery from poor processing oil sand ores. The oily bubbles were added, in a pipeline loop during bitumen liberation from the oils sands. The bitumen recovery from a poor processing ore with the addition of the oily bubbles to the conditioning slurry was found to be comparable to that of good processing ores.

Miller et al. (2004) analyzed the contact time between the gas bubbles and bitumen and emphasized that the attachment of bitumen to a gas bubble and the kinetics of bitumen spreading over the bubble surface should be rapid in order to guarantee an efficient separation process. The results of their study indicated that the transfer of the viscous bitumen from a quartz surface to an air bubble was a relatively slow process at room and moderate temperatures indicating that the bitumen-transfer process might significantly limit the flotation of viscous bitumen from the oil sands. Elevated temperatures significantly enhanced the bitumen transfer from the quartz surface to the air bubble. This resulted in a conclusion that the reduction of the bitumen viscosity seems to be the means for improved bitumen recovery from oil sands. This observation is consistent with the technological criteria established in the past (Hupka et al., 1987; Hupka and Miller, 1991). Hupka et al. (1983) suggested an excellent correlation between the separation efficiency and bitumen viscosity. Hence, it is evident that using a solvent to reduce the viscosity of bitumen and hence to increase bitumen recovery is of significant importance.

Zhou et al. (2005) studied the role of acidified sodium silicate addition as a dispersant/depressant of clay fines in bitumen extraction using a laboratory hydro transport extraction system (LHES) at low temperature operation (35°C). The experimental results indicated that the addition of acidified silicates during the bitumen extraction not only resulted in a higher degree of bitumen liberation from sand grains but also resulted in faster bitumen flotation rate and a better bitumen froth quality as compared to the results obtained for caustic addition. The reason for a better activity of silicates was identified by analyzing the solution chemistry, which demonstrated that acidified sodium silicate is a better process aid as compared to caustic because of the three functions observed for silicates. First, it precipitated calcium and magnesium in the process water to minimize the synergistic effect of divalent cations in inducing a clay coating on the bitumen surface and clay gelation; second, it maintained an adequate pulp slurry pH for better bitumen-air bubble attachment; and third, it dispersed / depressed the clay fines from flotation.

Su et al. (2006) studied the effect of solvents on induction time of bitumen–bubble attachment, using oily bubbles for three different types of solvents viz kerosene, toluene and heptane. The experiments demonstrated that bitumen flotation recovery from these ores could be greatly enhanced by using oily bubbles (air bubbles coated with a thin layer of oil or solvent) instead of air bubbles. The use of solvents increased spreading of three-phase contact lines reflected by a reduced induction time of air bubbles attaching to bitumen surfaces. In this study, dynamic contact angle of air/oily bubbles on bitumen surface and induction time of bitumen-air/oily bubble attachment in aqueous solution were measured to investigate the mechanism of how oily bubbles help improve bitumen recovery and justify the use of oily bubbles while processing poor oil sand ores. It was observed that the type of solvent used in generating oily bubbles showed a marginal effect on the receding contact angle values, similar to the values measured with air bubbles. However, the spreading on a bitumen surface of an air bubble was found to be much slower than that for oily bubbles. Induction time was found to be more sensitive than contact angles to the changes of bitumen flotation system, including changes in ore grades, water chemistry and surface properties of the air bubbles. In the process water from poor processing ores, the induction time for oily bubble–bitumen attachment was found to be much shorter than that for air bubble–bitumen attachment. The reduced induction time for kerosene-coated air bubble-bitumen attachment correlates well with the improved bitumen recovery from poor processing ores using kerosene-coated oily bubble flotation technology.

2.6. MORPHOLOGY ANALYSIS OF BITUMEN FROTH:

Schramm et al. (1998) conducted imaging experiments to observe the changes in the emulsified water drop sizes or shapes in the froth upon addition of the solvent in the nascent froth. Separate extraction/flotation experiments were conducted for the base case without solvent addition and with the addition of 4-ml of 2-propanol to the nascent froth. The froth sample without any solvent addition as well as that obtained using 2-propanol addition in the froth was imaged using magnetic resonance imaging (MRI) and CAT-scan for a greater resolution of the water droplets in both samples. Both images were obtained using identical MRI instrument settings and at the same time after sample collection. Since the addition of 2-propanol in the nascent froth led to lower water content in the froth, the images from the two cases reflected this reduction in water content. They advocated that the higher droplet density visible in the case of control sample image was consistent with higher water content found in the control extraction froth. The lower droplet density visible in the 2-propanol treated froth was consistent with the lower water content found in the treated froth. The control extraction froth droplets tended to be quite close to spherical in shape and the 2-propanol treated froth droplets tended to be quite angular in shape suggesting strong interfacial films.

Munoz et al. (2003) studied bitumen froth morphology for the identification of problem oil sand ores using confocal microscopy. Froth from different types of ores was analyzed using Confocal Laser Scanning Microscopy (CLSM). The CLSM technique used for the analysis combines some features of Light Microscopy (LM) and scanning electron microscopy (SEM), wherein the froth sample is scanned point-by-point with a finely focused laser beam. The investigation was carried out using samples from commercial oil sands extraction operations as well as from controlled laboratory extraction tests. The results from their research indicated that microscopic characterization of froth samples from poor processing ores showed distinctive microscopic features that were not present for good processing ores. These features included distinctly different fluorescence behavior for bitumen in the froth and completely different froth morphology for poor as well as degraded ore. They suggested that the different types of microscopic structures in the microscopic images identify the resulting change due to oxidation of bitumen phase. Differences in froth structure observed on a micro-scale illustrate the chemical complexity of the bitumen component in oil sands. The analysis demonstrates that the bitumen in an oil sand ore is the phase that is most susceptible to oxidation.

The morphological features found in froths of oxidized ores have been categorized and quantified. They are referred to as degraded bitumen structures. Experiments in which fresh oil sand ores were subjected to low-temperature oxidation showed that bitumen froth morphology changed dramatically compared to that of non-oxidized ores for identical bulk compositions and extraction water chemistries. Figure 2.3 is a microscopic image of bitumen with low fluorescence and normal fluorescence.

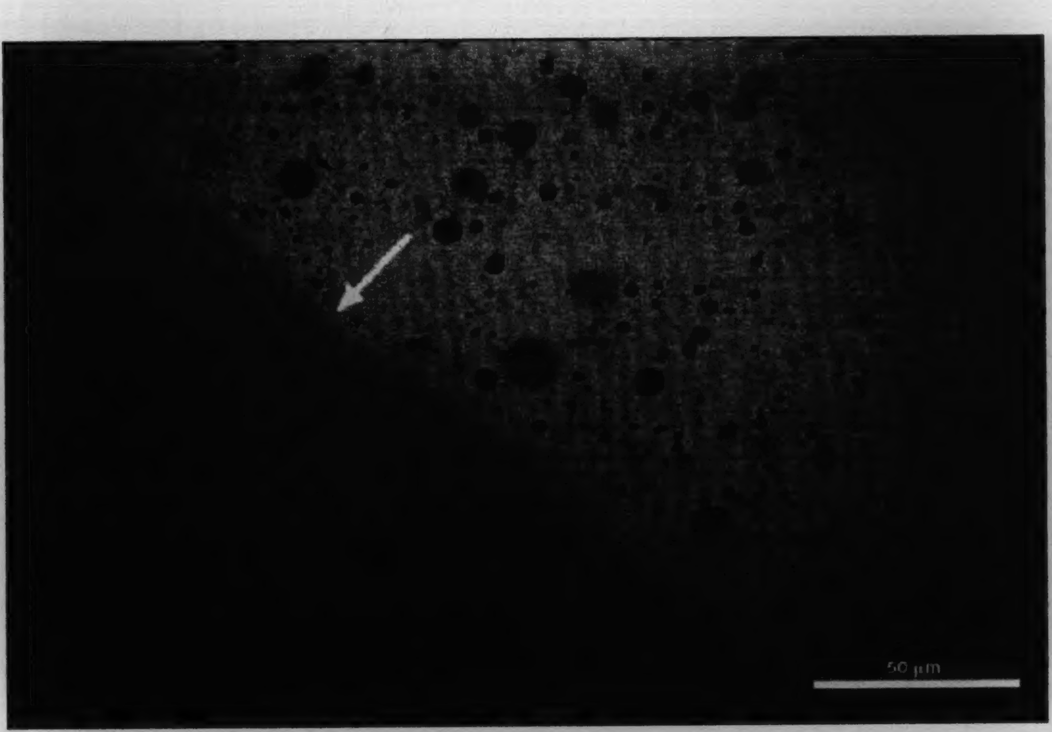


Figure 2.3: Confocal micrograph of bitumen froth from good processing ore showing an area of higher and lower fluorescence intensity (arrow). (Munoz et al. 2003)

The low-fluorescence area (arrow) has been attributed to the differences in the chemical composition as compared to the normal bitumen (top right). The dark circles in the continuous phase correspond to water droplets. Apart from some water droplets, the bitumen shown on the upper right side of the micrograph is featureless, which has been defined as an attribute of normal good quality bitumen. On the other hand, the formation of various characteristic structures is the most definitive indicator of the presence of degraded bitumen in froth. A classification of many shapes and sizes of the structures is also presented in the study. Figure 2.4 is a confocal micrograph of froth from an oven-oxidized good processing ore from Athabasca (13 wt. % bitumen, 2 wt. % water, and 85 wt. % solids), which was oven-dried for 42 hours at 50°C for oxidation experiments.

Figure 2.4: Confocal micrograph of a froth from an oven-oxidized ore (Oxidized for 42 h at 50°C) (Munoz et al. 2003)

The confocal micrograph of the froth from an oven-oxidized ore showed a dramatic increase in degraded bitumen structures. It was identified that most of these structures were over 250 mm in size and three-dimensional in shape. The increase in degraded bitumen structures in the oxidized ore froth was estimated to increase to 90-95 vol. % as against the froth from the fresh ore that showed less than 5 vol. % degraded bitumen structures. It has been advocated that the structures found in the oven oxidized ore are similar to those observed in the micrographs of the naturally occurring degraded bitumen and rag layers formed during oil sand processing. From the investigation based on the image analysis of the bitumen froth, it has been summarized that quantification of the microscopic morphology of oil processing emulsions can be used as a quick method for assessing the nature of the oil or bitumen surface and ore processability.

3. SOLVENT WASHING OF FROTH

3.1. JAR TEST WITH BITUMEN FROTH AND SOLVENTS

3.1.1. EXPERIMENTAL PROCEDURE

Preliminary experiments were carried out using a jar test method to observe the impact of solvent washing of the bitumen froth. The following steps were followed as the experimental procedure for all the experiments:

- 300 g of homogenized ore were used for all of the experiments. After removing from the freezer, the bagged ore was left on the laboratory bench for 3-4 hrs prior to bitumen extraction using Denver cell.
- 950 ml of Aurora process water of an average pH of 8.2-8.8 was used in all the experiments and bitumen extraction was carried out at 50°C maintained by the Denver flotation cell jacket and a thermal bath.
- Process water was added in the 1-liter jacketed flotation vessel of the Denver cell. Water circulation was started in the jacketed flotation vessel to maintain the desired temperature. Denver cell agitator was started and run at 1500 rpm without airflow and oil sand ore was added to the process water after the water attained the desired temperature. The agitator was run for first 5 minutes after ore addition to homogenize and condition the oil sand slurry followed by introduction of air at 150 ml/min.
- Air addition initiated froth generation, which was continuously scooped for the next 10 minutes and the removed froth from the Denver cell was placed in a glass container.
- Representative sample of 10 g of froth was taken in each of the three 200 ml jars and 100 ml of process water at room temperature was added to each jar for froth dilution.

All the three jars were shaken in standard shaker at low speed for 5 minutes. They were labeled jar 1 to jar 3.

- No solvent was added in jar 1. 2ml of kerosene was added to the slurry in jar 2 and 2ml of naphtha was added to the slurry in jar 3. All the three jars were again shaken for 1 minute. After this procedure, the jars were left undisturbed for 1 day to allow phase separation.

3.1.2. OIL SAND ORES AND SOLVENTS USED

Only kerosene and naphtha were used for this set of experiments. The characteristics of oil sand ores used for solvent washing of froth using the jar test procedure are given below:

Table 3.1: Oil sand characterization of the ores used for jar test solvent wash experiments

Oil Sands	**Composition (Wt. %)**			
	Bitumen	**Water**	**Solids**	**Fines#**
Poor processing ore*	5.8	5.9	87.6	36.3
Average grade ore**	10.1	3.4	86.2	10.9

* From Syncrude ** From Suncor # Wt. % of Total Solids

3.1.3. RESULTS AND DISCUSSIONS

Figure 3.1 shows the phase separation observed for poor processing ore froth after 1 day of phase separation for naphtha and kerosene washed froth as compared to the base case slurry without solvent wash.

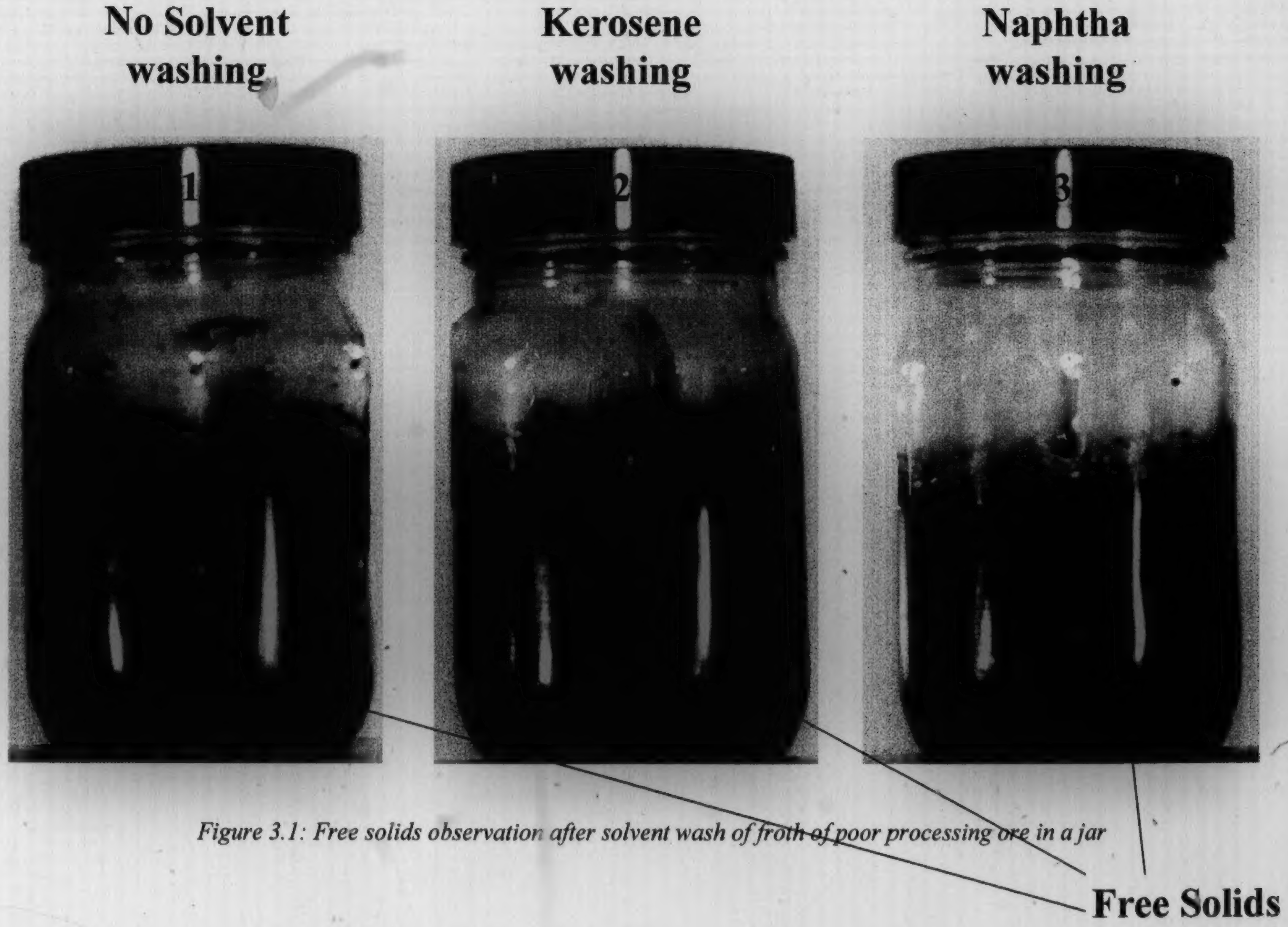

No Solvent washing
Kerosene washing
Naphtha washing
1
2
3
Free Solids

Figure 3.1: Free solids observation after solvent wash of froth of poor processing ore in a jar

The distinct layer of solids separated from bitumen froth in Figure 3.1 shows that the naphtha and kerosene washed froth slurry from poor processing ore showed better separation of solids from the bitumen froth as compared to the base case in which no solvent was added. Similar results were observed for the average grade ore with respect to better phase separation due to solvent addition.

The froth accumulated at the top of the three jars were removed carefully after settling period of 24 hours. The froth was further analyzed for composition using Dean Stark Analysis. Figure 3.2 shows the results for solids to bitumen ratio for the two types of ores.

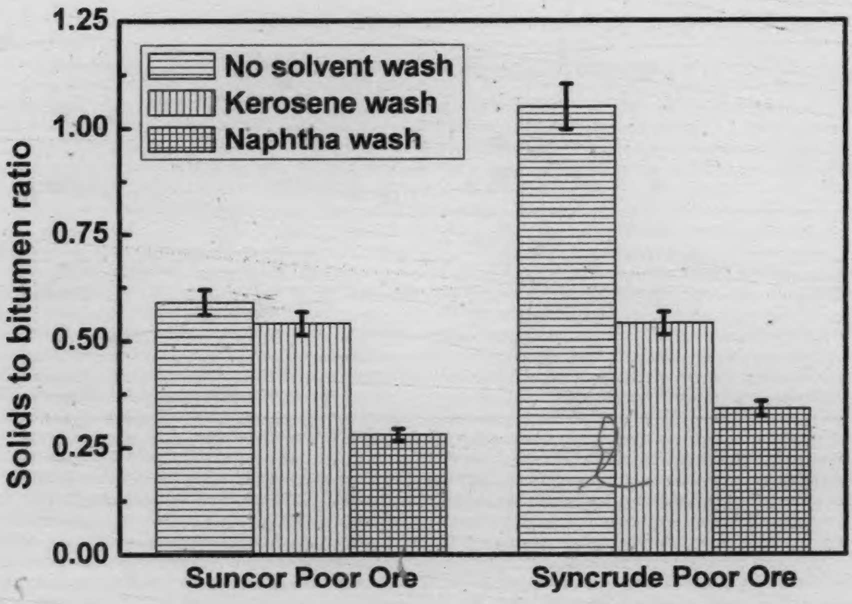


Figure 3.2: Solids to bitumen ratio after solvent wash in a jar test at 50^{0}C extraction

The froth composition results indicate reduction in solids to bitumen ratio by solvent wash for both types of ores. As shown in Figure 3.2, solids to bitumen ratio in the froth washed with kerosene and naphtha is less as compared to the base case in which no solvent was added. The results also show that the effect of solvent wash is more pronounced in poor processing ore froth as compared to average grade ore.

3.2. SOLVENT WASHING OF THE FROTH DURING FROTH GENERATION IN THE DENVER CELL

3.2.1. EXPERIMENTAL PROCEDURE

After the positive results of the jar tests with respect to reduction in solids content as well as solids to bitumen ratio, a set of experiments was carried out wherein solvent addition was carried out on the froth during froth generation in the Denver cell. The procedure used for this set of experiments was carried out to simulate the solvent addition/ washing of froth during froth generation at the primary separation vessel (PSV) stage in the commercial operation. The following experimental procedures were followed as the:

- 300 g of homogenized ore were used for all the experiments. After removing from the freezer, the bagged ore was left on the laboratory bench for 3-4 hrs prior to bitumen extraction using Denver cell.
- 950 ml of Aurora process water of an average pH of 8.2-8.8 was used in all the experiments and bitumen extraction was carried out at 50°C maintained by Denver flotation cell jacket and a thermal bath.
- Process water was added in the 1-liter jacketed flotation vessel of Denver cell. Water circulation was started in the jacketed flotation vessel to maintain the desired

temperature. Denver cell agitator was started and run at 1500 rpm without airflow and oil sand ore was added to the process water after the water attained the desired temperature. The agitator was run for first 5 minutes after ore addition to homogenize and condition the oil sand slurry followed by introduction of air at 150 ml/min.

- After introducing air, solvent addition (kerosene or naphtha) was carried out using a 10 ml glass syringe or a Qorpak chemical sprayer bottle on the froth as the froth generation started during 1st minute of air addition. This step was followed by 2 minutes of solvent dispersion into the froth. Hence during these initial three minutes, no froth was collected. After initial 3 minutes, froth was continuously scooped for the next 7 minutes.
- Hence the procedure involved, conditioning of slurry for 5 minutes followed by air introduction, solvent addition in the 6th minute (one minute), solvent dispersion in 7th and 8th minute (two minutes), and finally removal of solvent washed froth during 9th to 15th minute (seven minutes).
- The solvent washed froth thus collected was further analyzed for bitumen, solids and water content using Dean Stark Analysis.

3.2.2. OIL SAND ORES AND SOLVENTS USED

Oil sand ores: The following five different types of oil sand ores were used for experiments in which the solvent washing of the froth was carried out during froth generation using a sprayer or syringe:

- High fines ore from Albian Energy Inc
- Poor processing ore from Syncrude
- Naturally weathered poor processing ore from Suncor

- Good processing esturine ore (F11B) from Syncrude North mine
- Artificially weathered good processing ore: Good processing ore, F11B, was artificially weathered in a controlled environment in an oven for 1 week under airflow and at a temperature of 50°C. A desired amount of oil sand was placed in an alumina tray as a 0.8 –1.0 cm thick layer and was placed in the oven where temperature of 50°C was already maintained. Airflow into the oven started after putting the alumina trays into the oven and was maintained at the same rate at 50°C for 7 days. The sample was removed from the oven after 7 days, cooled down to room temperature and used for bitumen extraction within 1-2 hours.

The characterization of the five types of ores used for the solvent wash experiments is given in table 3.2.

Table 3.2: Oil sand characterization of the ores used for solvent wash during froth generation

Oil Sands		Composition (Wt. %)			
		Bitumen	**Water**	**Solids**	**Fines***
A	**High fines ore**	13.8	3.9	82.1	45.2
B	**Poor processing ore**	5.8	5.9	87.6	36.3
C	**Naturally weathered poor processing ore**	7.5	6.8	85.2	2.3
D	**Good processing ore**	14.6	2.2	82.7	2.1
E	**Artificially weathered good processing ore**	13.7	0.5	85.8	2.1

* Wt. % of total solids

Solvents: Following solvents were used for these sets of experiments where solvent washing of the froth was done during froth generation:

- Kerosene: Laboratory grade K10-4 from Fisher Scientific
- Naphtha: Commercial grade from Syncrude
- Kerosene mixed in wash water (30 ml of process water)
- Naphtha mixed in wash water (30 ml of process water)

The results obtained for solids to bitumen ratio in froth recovered for different cases were compared to the base case in which no solvent was added or only 30 ml of process water was added.

3.2.3. RESULTS AND DISCUSSIONS

3.2.3.1. EFFECT OF QUANTITY OF SOLVENT:

The first set of experiments was carried out using high fines ore and all the four types of solvents given in section 3.2.2. Solvent was injected uniformly on the top of froth during froth generation in Denver cell using the syringe for naphtha and kerosene and using chemical spray bottle for naphtha and kerosene mixed in 30 ml process water (wash water). The quantity of kerosene and naphtha used in these experiments was 3ml, 6ml and 9ml, respectively. Similarly 3ml, 6ml and 9ml of kerosene and naphtha, respectively in 30 ml of process water were added to observe the impact of washing with a solvent in process water on the solids to bitumen ratio in the recovered froth. Figure 3.3 shows that the solids to bitumen ratio decreased with the addition of solvents and the reduction increased with an increase in solvent quantity. Maximum reduction in solids to bitumen ratio was observed in case of pure naphtha and kerosene. Similar results were observed in other two cases in which solvents mixed with process water were used.

However, the reduction was less as compared to the case with respective pure naphtha and kerosene addition cases. It is worth to mention that for high fines ore spray wash of 30 ml process water without any solvent addition also reduced the solids to bitumen ratio from around 1.7 to 1.5 as is clear from point A and B on y axis (corresponds to 0 ml solvent). Point A corresponds to solids to bitumen ratio of a case for no solvent addition, while point B here corresponds to 30 ml wash water (process water) injection without any solvent.

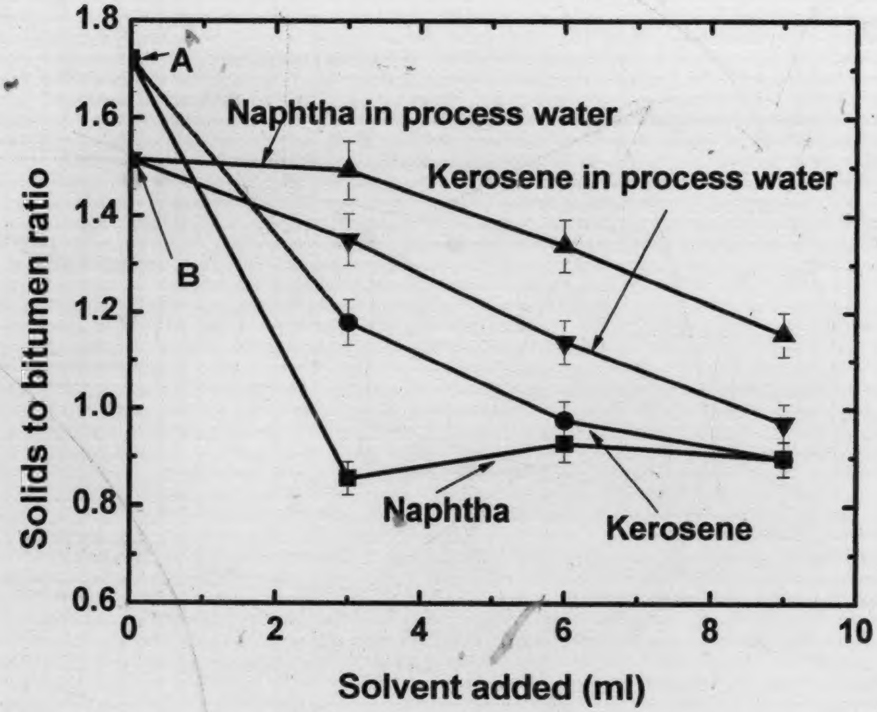


Figure 3.3: Solids to bitumen ratio for high fines ore froth for solvent washing of froth during froth generation in a Denver cell at 50°C extraction

3.2.3.2. EFFECT OF MODE OF SOLVENT ADDITION

The effect of mode of solvent addition was checked using 2ml, 4ml, and 6ml naphtha as a solvent and a poor processing ore extraction at 50°C. In the first case, naphtha was uniformly injected using a syringe and in the second case, naphtha was uniformly sprayed on the top of froth during froth generation from poor processing ore using Quorpak chemical sprayer bottle from Fisher. The Quorpak sprayer bottle (Figure 3.4) has an adjustable nozzle, which can be calibrated for fine mist to coarse spray of solvent for uniform distribution of solvent in the froth.

Figure 3.4: Quorpak chemical spray bottle with adjustable nozzle for fine mist spray used for solvent spray on froth during froth generation in Denver cell

Figure 3.5 shows that the extent of reduction in solids to bitumen ratio was found to be similar for spray washing and washing by syringe. From this set of experiments it was concluded that the effect of solvent addition on reduction in solids is independent of mode of addition, though using spray has better control on uniform distribution of solvent in the froth. Hence, all the experiments carried out and discussed thereafter are based on the tests in which solvent washing of froth during froth generation was carried out using the Qorpak chemical spray bottle.

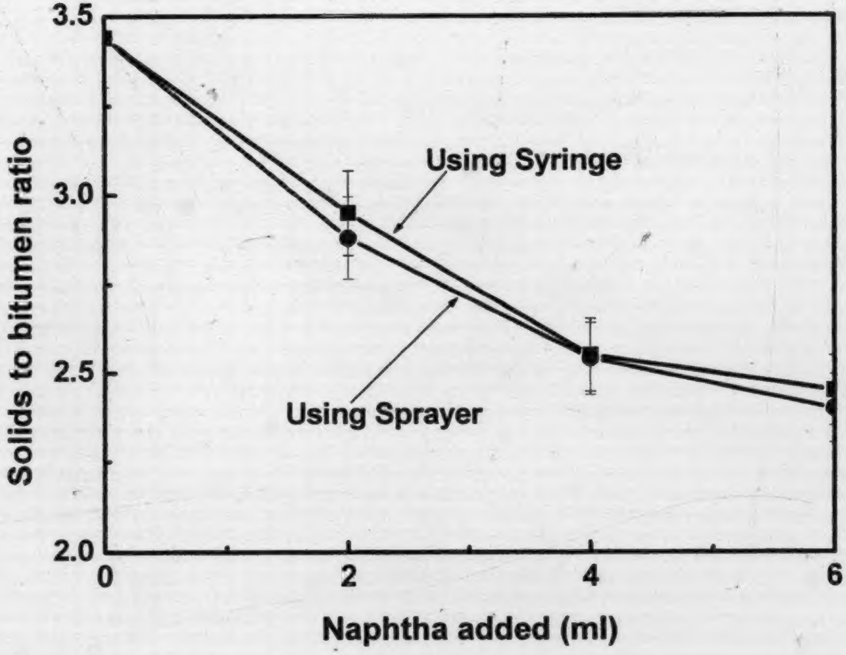


Figure 3.5: Solids to bitumen ratio for a naphtha washed poor processing ore froth using syringe and sprayer during froth generation in a Denver cell at 50°C extraction

3.2.3.3. EFFECT OF WEATHERING OF ORE

In this set of experiments, solids to bitumen ratio for poor processing ore froth and naturally weathered poor processing ore froth with 2 ml, 4ml and 6 ml naphtha spray washing is compared to the base case of no solvent wash at 50°C extraction. Figure 3.6 shows that for the poor processing ore, solids to bitumen ratio decreased with the addition of naphtha. However for the naturally oxidized / weathered poor processing ore, the solids to bitumen ratio did not show any regular pattern in response to the addition of higher quantities of solvent.

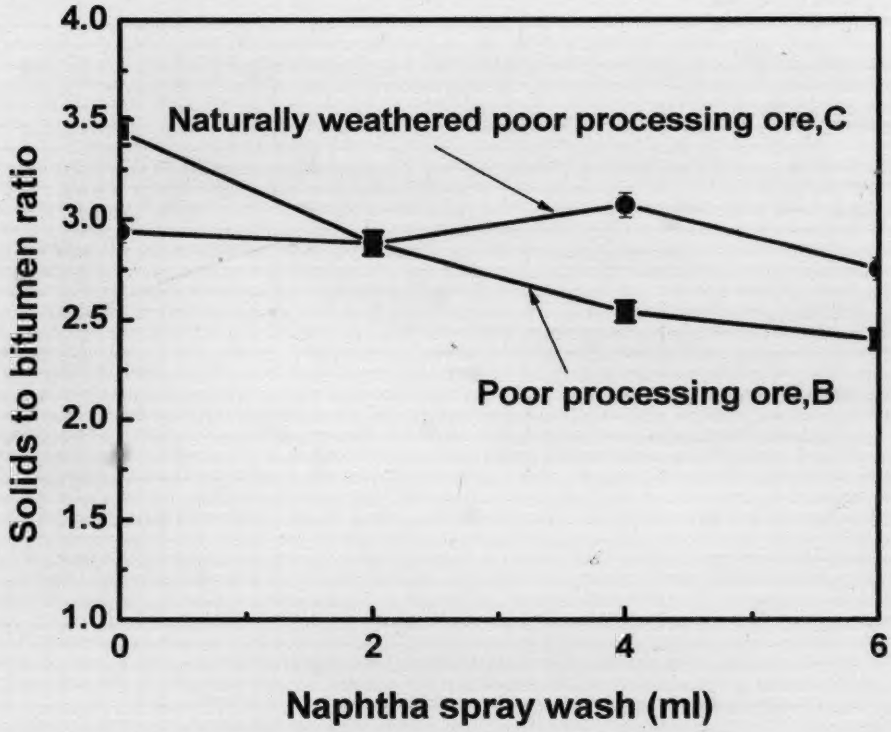


Figure 3.6: Solids to bitumen ratio for naphtha washed froth using sprayer during froth generation in a Denver cell at 50°C extraction for poor processing ore and naturally weathered poor processing ore

The results obtained for the poor processing ore as shown in Figure 3.6 indicates gradual decrease in solids to bitumen ratio with the addition of naphtha but for weathered poor processing ore, the results are not conclusive. Figure 3.7 shows the comparison of results obtained for good processing ore and the artificially weathered good processing ore. It was noted that solids to bitumen ratio remained the same for good processing ore due to very small quantity of solids in the froth, but for artificially weathered good processing ore solids to bitumen ratio showed irregular pattern in response to naphtha addition, in some cases it was even found to increase.

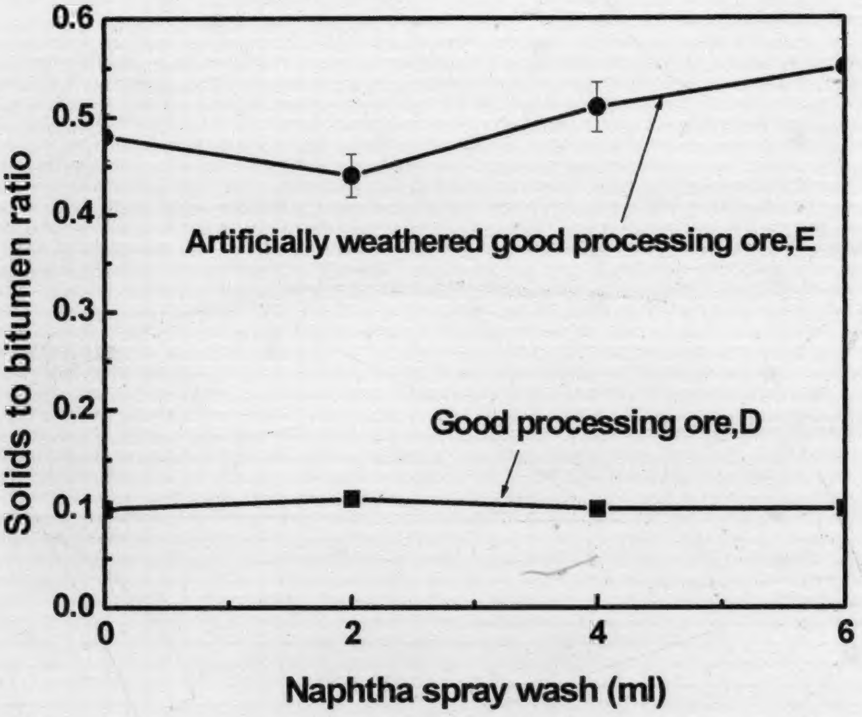


Figure 3.7: Solids to bitumen ratio for naphtha washed froth using sprayer during froth generation in a Denver cell at 50°C extraction for good processing ore and artificially weathered good processing ore (Weathered for 1 week at 50°C in an oven under air flow)

Another noticeable point is that the solids to bitumen ratio increased by more than four times for the good processing ore from the level of 0.1 to around 0.48 due to weathering. This increase in the solids to bitumen ratio is due to the increase in the solids in the froth as well as the decrease in the bitumen recovery due to weathering of the ore. This observation is in line with the studies carried out previously on weathered ores in which significant loss of bitumen recovery has been concluded. This set of experiments implies that weathering of ore not only leads to loss of potential bitumen recovery but also leads to lower levels of solids separation from bitumen during extraction.

3.2.3.4. EFFECT OF OPERATING TEMPERATURES

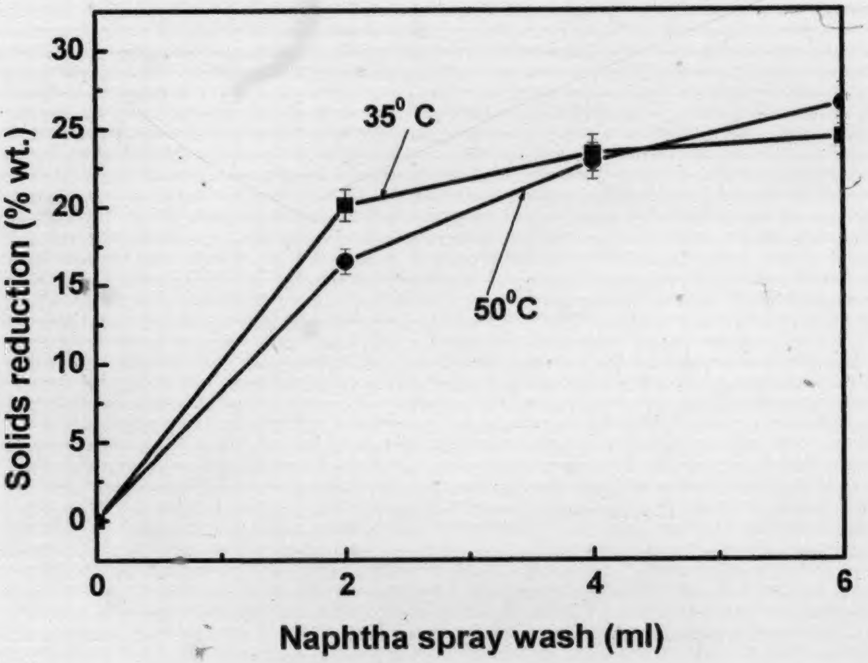


Figure 3.8: Percent reduction in solids in naphtha washed froth using sprayer during froth generation in a Denver cell at 50°C and 35°C extraction for poor processing ore

In this set of experiments, the effect of operating temperature was checked using naphtha spray washing of the froth during froth generation from a poor processing ore. Till now all the experiments were carried out at 50°C operating temperature. A set of experiments was carried out at 35°C and comparison of the percent reduction in solids in the recovered froth was done for both the temperatures. Figure 3.8 shows the results for both the cases. It was observed that at 50°C the reduction in solids was uniform with the addition of naphtha, but for 35°C operation, the reduction in solids was observed to be highest at initial 2 ml addition of naphtha but with higher addition of naphtha the extent of solids reduction was less than what was observed at 50°C. However, significant observation is that upto 25% reduction in solids was achieved for 6 ml naphtha wash of poor processing ore froth at both operating temperatures.

3.3 PARTICLE SIZE DISTRIBUTION OF SOLIDS IN THE SOLVENT WASHED BITUMEN FROTH

The solids recovered in the froth were further analyzed for particle size distribution to observe the effect of solvent washing on the solids in the recovered froth. Particle size distribution analysis was conducted for solids recovered in the froth for different cases comprising 0 ml; 2ml, 4ml and 6ml naphtha spray washing of poor processing ore froth both at 50°C and 35°C extraction. The analysis of particle size distribution was carried out using the Syncrude Analytical method for determination of fines (< 45 μm particle size) distribution using wet screening method.

3.3.1 EXPERIMENTAL PROCEDURE:

The procedure used for the separation of solids from the recovered froth and segregating recovered solids into two size portions with +/- 45μm nominal diameter employs a wet screening technique. Following is a brief overview of the procedure used for analyzing particle size distribution:

- The solvent washed froth for different cases were generated and collected as per the procedure given in section 3.2.1. Instead of analyzing the froth samples using Dean Stark analysis, solids were separated using steps given below.
- Froth samples were transferred into 250 ml centrifuge FEP (Fluorinated Ethylene Propylene) bottles and filled to volume with a 50:50 toluene/isopropyl alcohol mixture. The bottles were mixed thoroughly for 10 minutes using a laboratory shaker at low speed and centrifuged at 33 rev/s for 20 minutes.
- After centrifugation, the extract comprising of water and bitumen dissolved in toluene was decanted carefully ensuring that no solids were lost. The bottles were refilled with toluene only and repeated the mixing, washing and centrifuging sequence until the decanted liquid in the bottle was colorless.
- At this stage, the centrifuge bottles containing extracted solids were half filled with isopropyl alcohol. The solids were dispersed in isopropyl alcohol by mixing with a spatula and transferring the slurry onto the sieve while gently tapping the sieve frame. The centrifuge bottles were rinsed with isopropyl alcohol until the effluent after passing the sieve and entering the beaker below the sieve was free of – 45 μm particles. This can be most easily checked by tipping the sieve and noting if particles flow down the inside rim.
- When complete, the sieve was removed from the funnel and dried for 2 hours. The sieve was cooled in desiccators and reweighed. The sieve effluent was evaporated to dryness in the oven and reweighed when cool.

3.3.2 RESULTS AND DISCUSSION

In this section, results obtained for particle size distribution of solids in naphtha washed recovered froth from poor processing ore at 35°C and 50°C are discussed. As discussed earlier, not only solids to bitumen ratio decreased in both the cases but also there was net decrease in the solids quantity in the recovered froth due to naphtha washing. Figure 3.9 and 3.10 shows the reduction in the total solids, fines and coarse solids in the recovered froth for the cases of 0ml, 2ml, 4ml and 6ml naphtha spray washed froth for 35°C and 50°C bitumen extraction respectively.

Figure 3.9 indicates that at 35°C extraction, maximum decrease in solid particles in solvent washed froth is observed at initial 2 ml addition of naphtha and thereafter the decrease is not much. Table 3.3 shows that percent reduction in solids at 35°C extraction is around 20% for 2 ml naphtha washing and further decreases by 2-4% for additional naphtha addition. However, Figure 3.10 indicates that at 50°C extraction, the decrease in the solids due to naphtha addition was higher for higher quantities. Table 3.4 shows that percent reduction in solids at 50°C extraction decreases gradually from 16% to 26% for 2ml, 4ml and 6ml of naphtha washing. Another important observation is that the decrease in the solids in case of 35°C extraction was mainly due to decrease in fines content in the solids and in case of 50°C extraction, the decrease in the solids was mainly due to decrease in coarse particles in the solids. Table 3.3 shows that at 35°C, of the overall decrease in solids of 20-24%, decrease in the fines was of the order of 30% and that of coarse particles was of the order of 3-13%. Table 3.4 shows that at 50°C, of the overall decrease in solids of 16-26%, decrease in the fines was of the order of 15-20% and that of coarse particles was of the order of 20-35%.

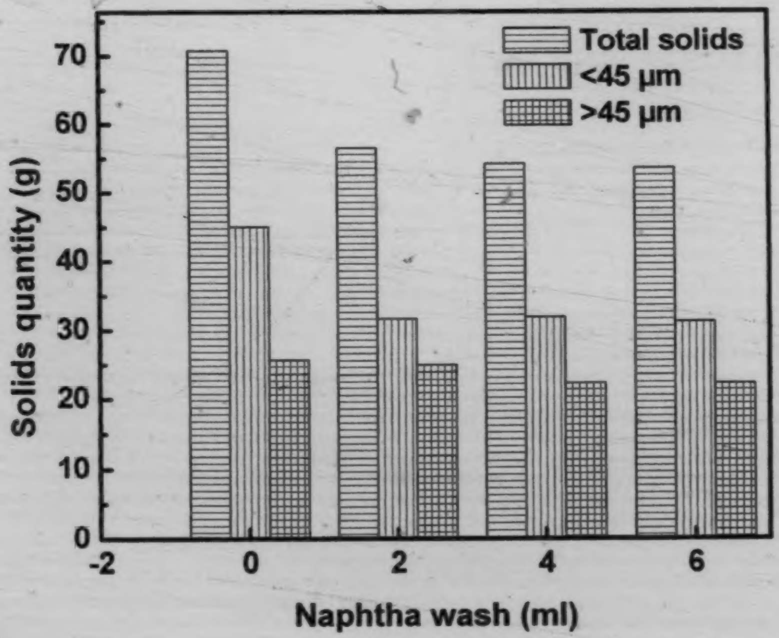


Figure 3.9: Particle size distribution of solids for the naphtha washed froth at 35°C extraction for poor processing ore

Table 3.3: Percent decrease in solids for the naphtha washed poor processing ore froth at 35°C extraction

Percent decrease in solids at 35°C extraction for poor processing ore	**Naphtha spray wash (ml)**		
	2 ml	**4 ml**	**6 ml**
Total solids	20.1	23.4	24.4
Fines	29.8	29.3	30.8
Coarse particles	3.1	13.0	13.0

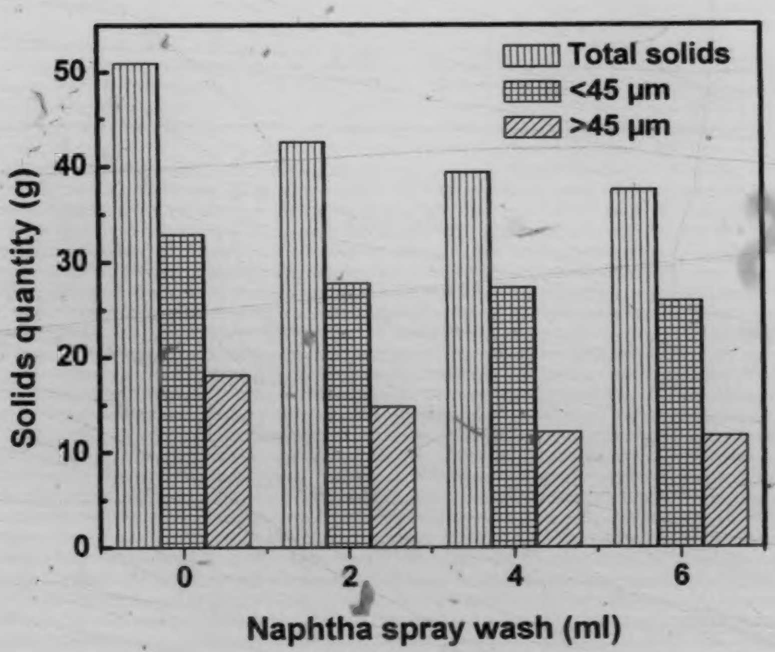


Figure 3.10: Particle size distribution of solids for the naphtha washed froth at 50°C extraction for poor processing ore

Table 3.4: Percent decrease in solids for the naphtha washed poor processing ore froth at 50°C extraction

Percent decrease in solids at 50°C extraction for poor processing ore	**Naphtha spray wash (ml)**		
	2 ml	**4 ml**	**6 ml**
Total solids	16.5	22.9	26.4
Fines	15.4	17.0	21.3
Coarse particles	18.4	33.4	35.9

The above analysis of higher reduction in coarse particles at 50°C extraction and that of fines at 35°C extraction due to naphtha washing of froth was also confirmed by further analysis of particle size distribution of fines particles. This was carried out using mastersizer. In this set of experiment, few grams of fines separated from the total solids extracted at 35°C and 50°C from poor processing ore were mixed in 50 ml of de-ionized water to make fine slurry. Few drops of this slurry was introduced in mastersizer to find the volume distribution of particles <45μm.

Figure 3.11 represents the results for particle size distribution of particles <45μm in solids recovered from poor processing froth at 50°C. For a 0 ml case i.e. no solvent washing case, the particle size distribution for particles <45μm on a plot of % Volume vs. particle size in μm shows two distinctive peaks. First peak indicates around 3.5% volume of particles around 0.1 μm i.e. lower size particle and second peak also indicates around 3.5% volume of particles around 40 μm i.e. higher size particle. For 2 ml naphtha washing case it is observed that the peak which indicates the volume % of particles around lower size particle (0.1 μm) increased from around 3.5% to more than 5% and the volume % of particles around higher size (40 μm) particle decreased from around 3.5% to less than 3%. Similar effects were observed in particle size distribution for 4 ml and 6 ml naphtha washing case as compared to base case.

This set of experiments for particle size distribution analysis of fines is another confirmation to the conclusion that at 50°C extraction, naphtha washing of froth led to decrease in coarser size particles to higher extent and at 35°C extraction, naphtha washing of froth led to decrease in fines to higher extent.

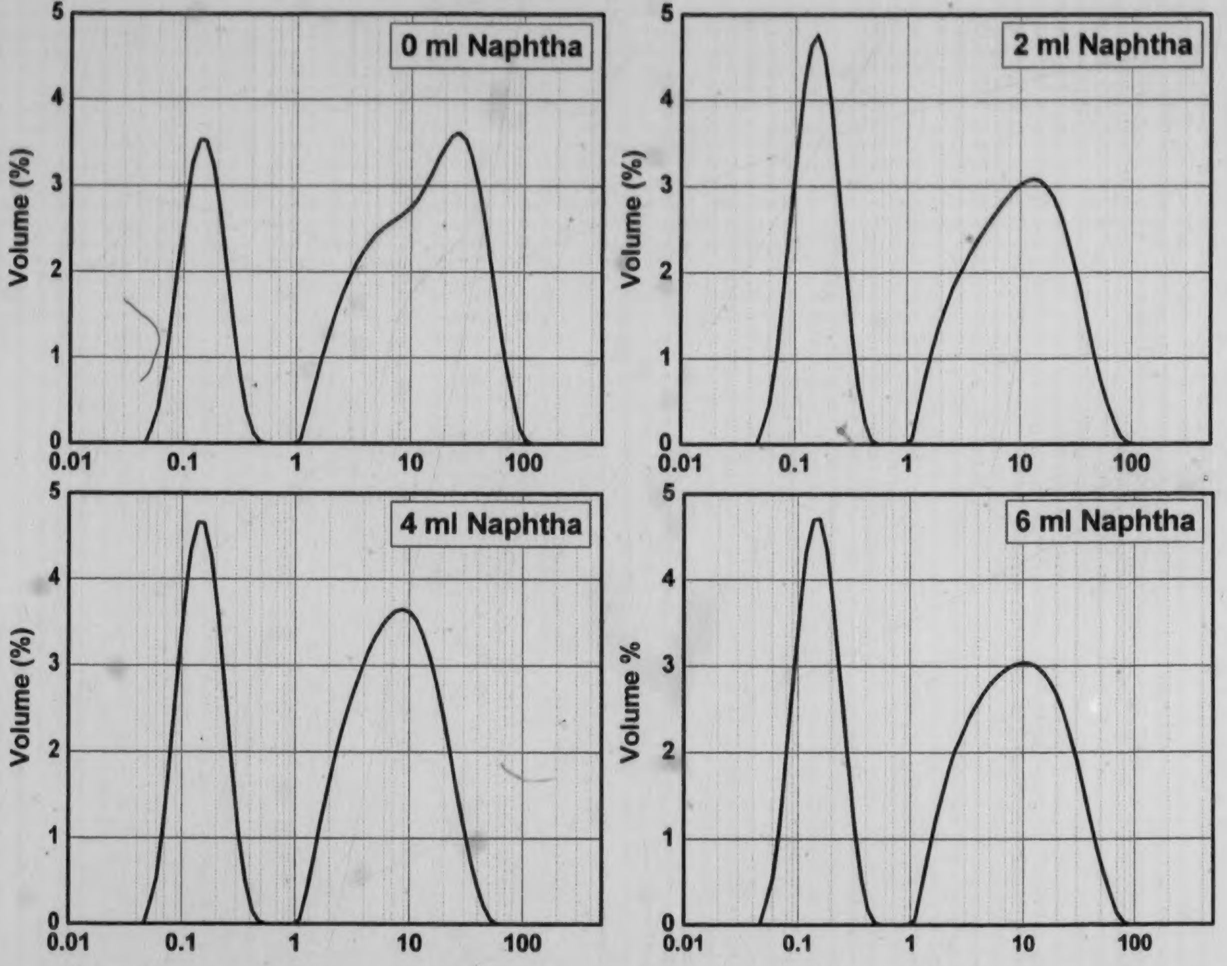


Figure 3.11: Particle size distribution in fines for naphtha washed froth of a poor processing ore at $50^{0}C$ extraction

3.4 IMPACT OF FROTH WASHING WITH OTHER SOLVENTS

3.4.1 HEPTOL (HEPTANE: TOLUENE:: 1:1)

The effect of heptol (heptane:toluene::1:1 volume) washing of froth was analyzed following similar steps as were used for naphtha and kerosene washing. The results for heptol washing vis a vis Naphtha shown in Figure 3.12 are similar with respect to reduction in solids to bitumen ratio for the poor processing ore at 50°C extraction.

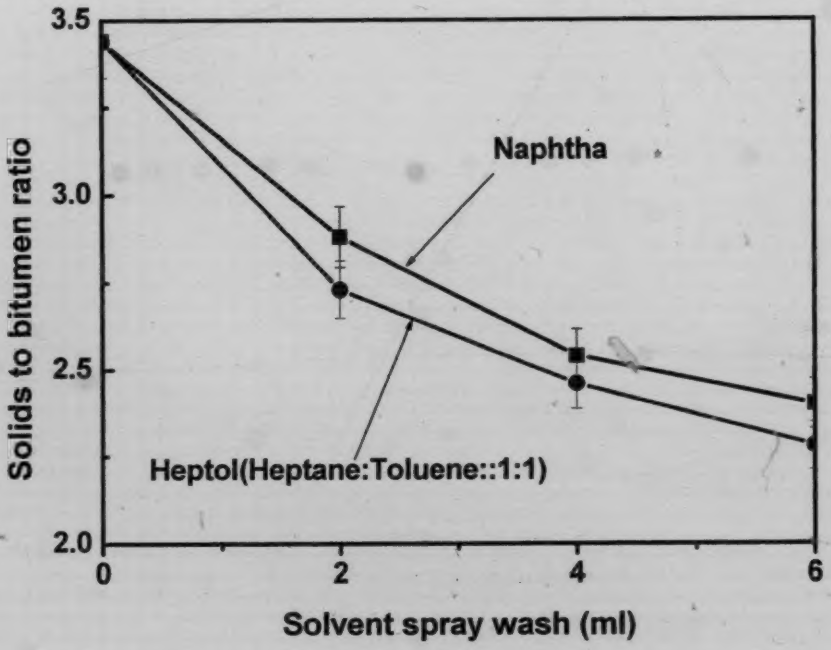


Figure 3.12: Solids to bitumen ratio for a solvent washed poor processing ore froth using sprayer during froth generation in a Denver cell at 50°C extraction for naphtha and heptol (heptane: toluene::1:1 volume)

3.4.2 OTHER SOLVENTS TOLUENE / PROCESS WATER /NAPHTHA IN PROCESS WATER

A set of experiments was also carried out for poor processing ore to observe the impact of washing of froth using other solvents like toluene, process water, and naphtha mixed in process water. However, in most cases no regular trends were observed with respect to improvement in bitumen recoveries or reduction in solids to bitumen ratio. Table 3.5 below gives the details of the results obtained for different solvents as a washing medium with poor processing ore at 50°C extraction.

Table 3.5: Bitumen recovery and solids to bitumen ratio for poor processing ore extracted at 50°C using different solvents for spray washing the froth during froth generation

Solvent	QTY Solvent (ml)	Bitumen Recovery	Solids /Bitumen	Froth Quality (%wt)		
				Water	Solids	Bitumen
Toluene	2	85.6	3.7	76.2	18.7	5.0
	4	85.8	4.0	76.5	18.8	4.7
	6	85.9	4.1	75.2	19.9	4.9
	2	83.9	3.6	76.6	18.3	5.1
	4	84.1	4.8	73.2	22.3	4.6
	6	84.9	3.5	77.6	17.5	5.0
Process Water	10	79.2	3.2	76.7	17.8	5.5
	20	81.9	3.1	78.9	15.9	5.2
	30	82.2	2.8	79.7	15.0	5.3
Naphtha in 30 ml process water	2	76.3	3.7	80.3	15.5	4.2
	4	74.5	3.7	79.4	16.2	4.4
	6	76.2	3.8	79.2	16.5	4.3

3.5 SUMMARY

Figure 3.13 summarizes the effect of naphtha in particular and kerosene, naphtha in general, on the impact of solvent washing on the reduction of solids in the froth for different ore types. The reduction in solids the after solvent wash is found to be highest in for high fines ores and appreciable for poor processing ores. In general, the reduction in solids increases with the increase in solvent dosage. The reduction in solids is negligible in case of weathered ores with no regular trend with an increase in solvent dosage and minimal in case of good processing ores.

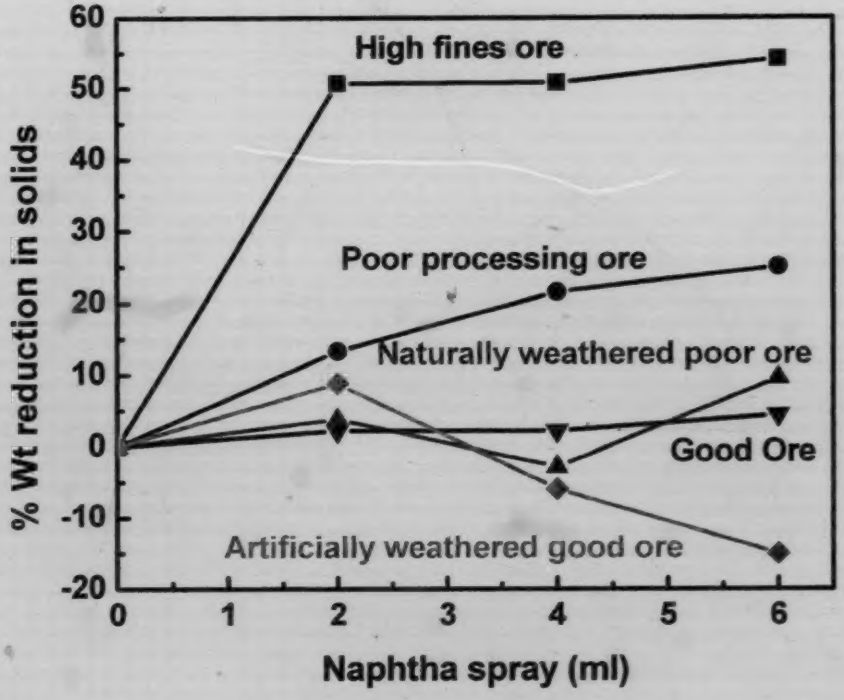


Figure 3.13: Percent reduction in naphtha washed froth using sprayer during froth generation in a Denver cell at 50°C extraction for different ores

4.0. SOAKING OF SOLVENTS IN OIL SAND ORE

4.1. IMPACT OF SOAKING OF SOLVENT IN OIL SAND ORE

As discussed in Chapter 3, solvent washing of froth showed positive results with respect to reduction in solids to bitumen ratio in the recovered bitumen froth. In view of the positive results, another set of experiment was carried out to observe the impact of soaking the solvent in the oil sand ore before extracting bitumen. Initial set of experiments which was carried out to compare the effect of soaking the solvent in the oil sand ore vis. a vis. solvent spray on the froth during froth generation using naphtha for two different poor processing ores showed that the results for soaking the solvent in the oil sand ore were better as compared to solvent washing of froth during froth generation.

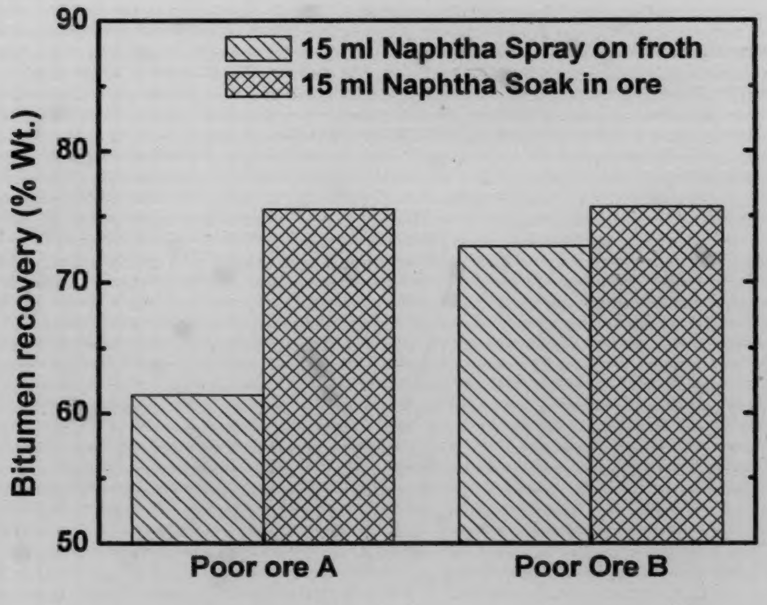


Figure 4.1: Comparison of bitumen recovery for poor processing ores for naphtha wash vs. naphtha soaking

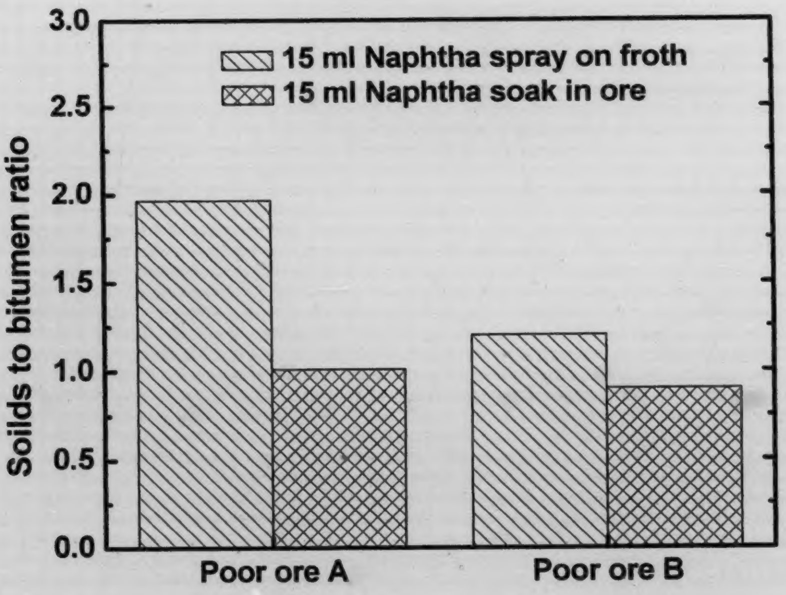


Figure 4.2: Comparison of solids to bitumen ratio for poor processing ores for naphtha wash vs. naphtha soaking

Figures 4.1 and 4.2 shows the comparison of bitumen recovery and solids to bitumen ratio, respectively for two poor processing ores at 50°C. In view of the better results for naphtha ore soaking, a set of experiments were carried to observe the effect of solvent soaking in the ore on bitumen recovery and solids to bitumen ratio for various types of ores at 50°C and 25°C extraction.

4.1.1 EXPERIMENTAL PROCEDURE

The initial set of experiments was based upon using naphtha as well as kerosene for soaking different types of ores followed by bitumen extraction at 50°C. Another set of experiments were conducted based on using only kerosene for soaking different type of ores followed by bitumen extraction at 25°C. The froth composition analysis was carried out using Dean Stark analysis to observe the impact on bitumen recovery and solids to bitumen ratio. The following steps were followed as the experimental procedure:

- 300 g of homogenized ore were used for all set of experiments. After removing from the freezer, the bagged ore was left on the laboratory bench for 3-4 hrs. The ore was removed from the bag and the fixed amount of solvent was added into the ore and continuous mixing of solvent in the ore was done for 1 minute. After this step, ore was set aside for solvent soaking in the ore for 5, 15 or 30 minutes prior to bitumen extraction using Denver cell.
- 950 ml of Aurora process water of an average pH of 8.2-8.8 was used in all the experiments. Bitumen extraction was carried out either at 50°C or 25°C maintained by Denver flotation cell jacket and a thermal bath.
- Process water was added in the 1-liter flotation vessel of Denver cell. Water circulation in the jacketed flotation cell was started to attain and maintain the desired temperature. Denver cell agitator was started and run at 1500 rpm without airflow and oil sand ore was added to the cell after the water attained the desired temperature. After adding the ore, the agitator was run for 5 minutes without air flow to condition the slurry followed by introduction of air @ 150 ml/min.
- After introducing the air, generated froth was continuously scooped off using spatula and collected for next 10 or 20 minutes. Froth was collected separately for first 2 minutes, next 3 minutes, 5 minutes and 10 minutes respectively in 3 or 4 separate thimbles. In most of the experiments at 50°C, 10 minutes of bitumen recovery was analyzed and at 25°C, 20 minutes of bitumen recovery was analyzed. The solvent

washed froth thus collected for different time periods was further analyzed for bitumen, solids and water content using Syncrude Dean Stark method.

4.1.2 OIL SAND ORES USED FOR THE EXPERIMENTS

The characteristics of oil sand ores used for the experiments discussed in this chapter are given below:

Table 4.1: Oil sand characterization of the ores used for ore soaking in the solvent

Oil Sands		**Composition (Wt. %)**			
		Bitumen	**Water**	**Solids**	**Fines***
A	**Poor processing ore (Syncrude)**	9.7	2.4	87.8	11.5
B	**Poor processing ore (Suncor)**	11.2	2.8	86.0	13.7
C	**Artificially weathered poor processing ore # (Syncrude)**	9.1	0.8	90.1	12.1
D	**Good processing ore (F11B)**	14.6	2.2	82.7	2.1

# Artificially weathered in an oven at 50°C under air flow for 1 week

* Wt. % on Total Solids

4.1.3 SOLVENTS USED FOR THE EXPERIMENTS

The experiments are based upon soaking 2 ml, 4ml, 6ml and 15 ml of naphtha or kerosene respectively in 300 g of different types of ores. Based on the % wt. bitumen content in different types of ores, these quantities of solvent in 300 g of ore corresponds to different levels of dosing as determined by solvent wt.% on bitumen quantity in a particular ore. Table 4.2 shows the amount of kerosene added as wt. % of bitumen in the ores used for the ores given in Table 4.1.

Table 4.2: Kerosene added as a percent weight of bitumen in the ore

Oil Sands		**Kerosene addition (wt.% of bitumen in the ore)**			
		2ml	**4 ml**	**6 ml**	**15 ml**
A	**Poor processing ore (Syncrude)**	5.5	11.0	16.5	41.2
B	**Poor processing ore (Suncor)**	4.8	9.5	14.3	35.7
C	**Artificially weathered poor processing ore (Syncrude)**	5.9	11.7	17.6	44.0
D	**Good processing ore (F11B)**	3.7	7.3	11.0	27.4

For example, 2 ml of kerosene in 300 g of poor processing ore-A (9.7% bitumen) corresponds to 5.5 wt. % of kerosene on the amount of bitumen in this ore. **In evaluating bitumen recovery, the amount of solvent added to the ore has been subtracted from the bitumen quantity in the recovered froth with the assumption that all of the solvent added with the ore is recovered in the bitumen froth.**

4.2 RESULT AND DISCUSSION FOR 50^{O}C EXTRACTION

4.2.1 IMPACT ON GOOD PROCESSING ORES

The effect of soaking kerosene in the good processing ore was checked for the ore D given in Table 4.1. Kerosene (0ml, 2ml, 4ml and 6ml case) was soaked in the ore for 15 minutes and extracted at 50°C for 10 minutes of bitumen recovery. The results for bitumen recovery and solids to bitumen ratio in Figure 4.3 shows marginal improvements for the cases in which kerosene was soaked in the ore as compared to the base case.

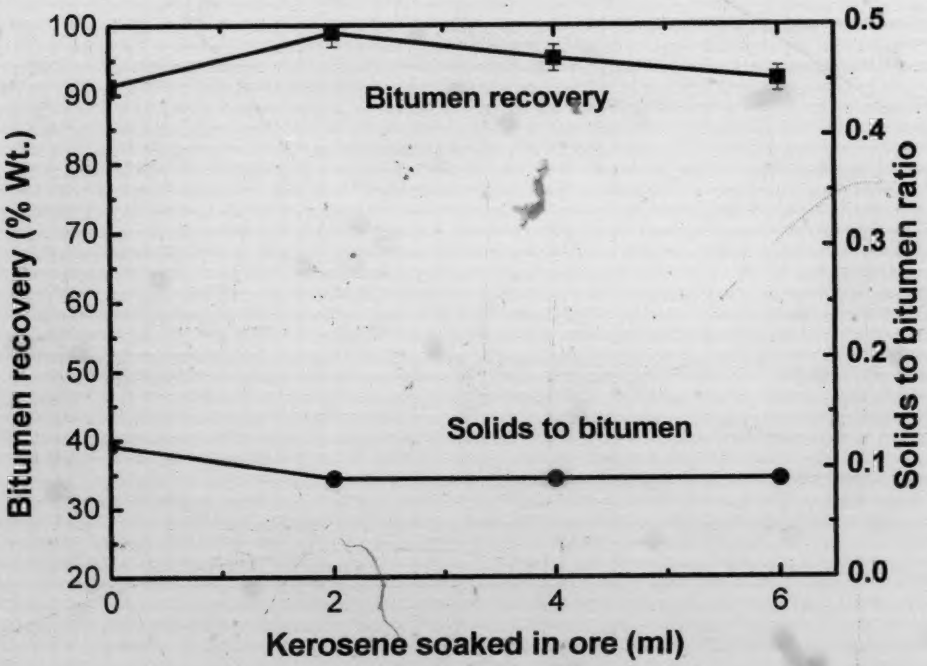


Figure 4.3: Bitumen recovery and solids to bitumen ratio for kerosene soaked in a good processing ore-D for 15 minutes and extraction done at 50°C for 10 minutes recovery

4.2.2 IMPACT ON POOR PROCESSING ORES

This set of experiments was carried out using two different poor processing ores i.e. ore A and B (Table 4.1). 2ml, 4ml, 6ml and 15 ml of either naphtha or kerosene was added in these ores and kept for 15 minutes soaking period prior to bitumen extraction. Figures 4.4 and 4.5 show the results of froth analysis for the bitumen recovery and solids to bitumen ratio variation for the poor processing ore A. Naphtha or kerosene soaking in the poor processing ore shows similar results with respect to bitumen recovery and solids to bitumen ratio at 50°C for both solvents.

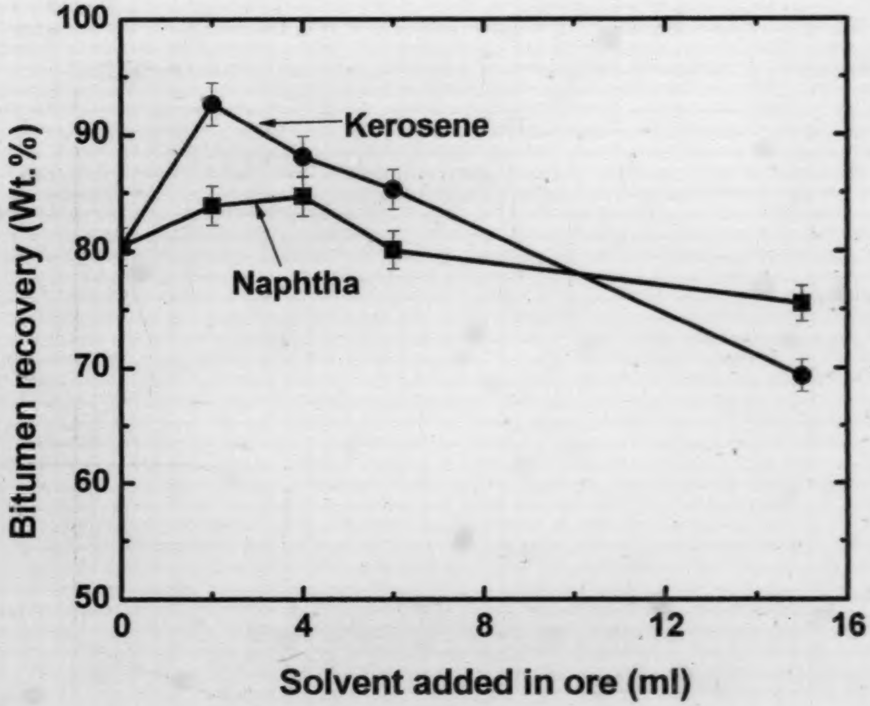


Figure 4.4: Bitumen recovery for solvent soaked poor processing ore-A soaked for 15 minutes and extraction done at 50°C for 10 minutes recovery

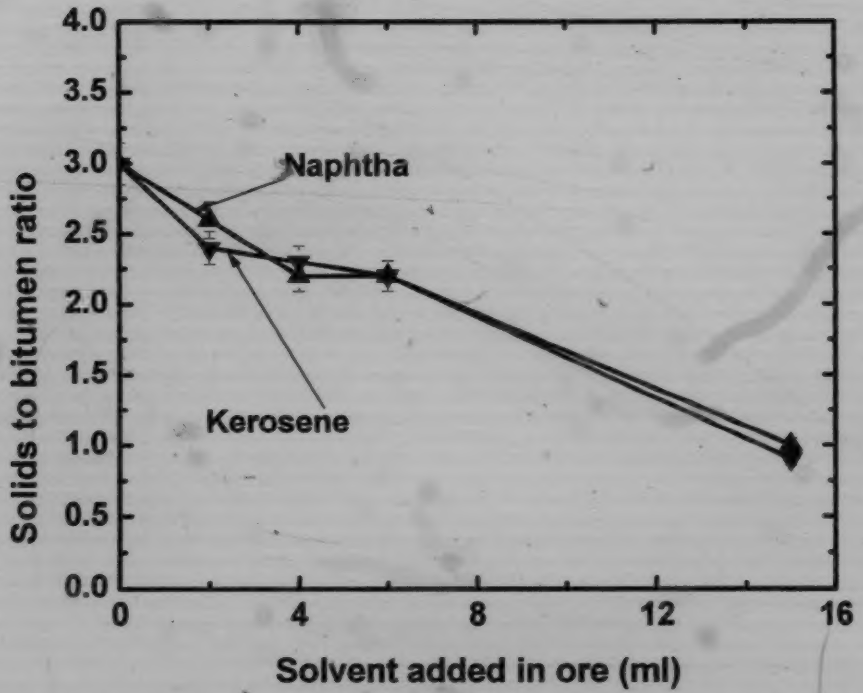


Figure 4.5: Solids to bitumen ratio for solvent soaked poor processing ore-A soaked for 15 minutes and extraction done at 50⁰C for 10 minutes recovery

Figure 4.4 shows that the bitumen recovery increases with the addition of solvent in the range of 0-2 ml and decreases there after at higher solvent addition. The solvent quantity added in the ore in this case has been subtracted from the total bitumen recovered in the froth. The decrease in bitumen recovery for higher levels of solvent addition (> 2ml) signifies that the incremental increase in the bitumen recovery is less as compared to the additional solvent added, which leads to a decrease in the net bitumen recovery. However as shown in Figure 4.5, solids to bitumen ratio decreased with the addition of both solvents. At 15 ml addition of both solvents for this particular ore, it decreases to about one third of the base case (down to around 1.0 from 3.0 for the base case). Figures 4.6 and 4.7 show similar results for poor processing ore- B.

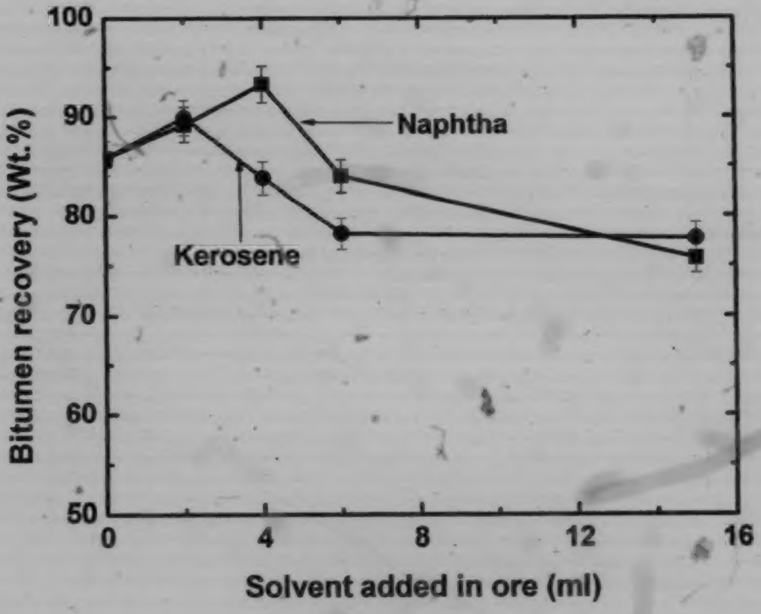


Figure 4.6: Bitumen recovery for solvent soaked poor processing ore-B soaked for 15 minutes and extraction done at 50°C for 10 minutes recovery

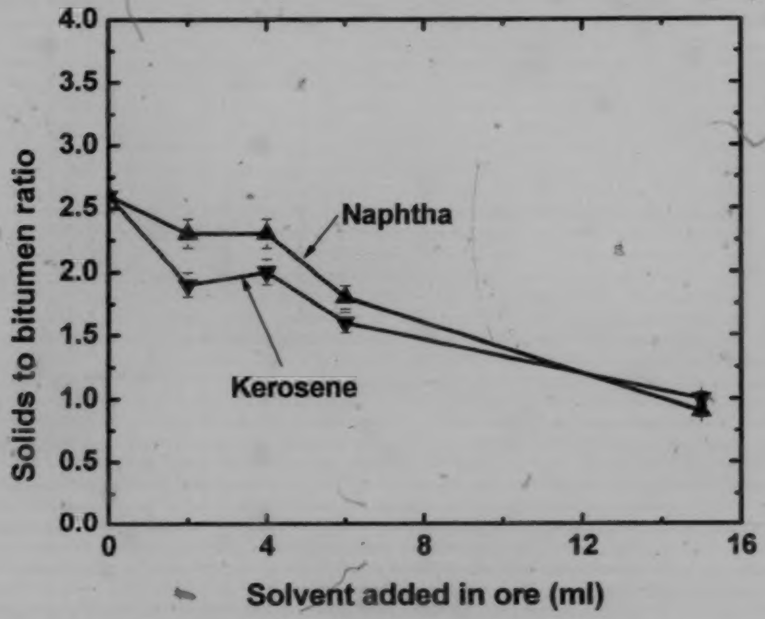


Figure 4.7: Solids to bitumen ratio for solvent soaked poor processing ore-B soaked for 15 minutes and extraction done at 50°C for 10 minutes recovery

4.3 RESULT AND DISCUSSION FOR 25°C EXTRACTION

A set of experiments was carried out to observe the impact of kerosene addition on the reduction of solids or solids to bitumen ratio as well as bitumen recovery at low temperature extraction of 25°C for good processing ore D, poor processing ore A and weathered poor processing ore C (Refer Table 4.1).

4.3.1 IMPACT ON GOOD PROCESSING ORES

For a good processing ore base case (without solvent addition) bitumen recovery corresponding to 10 minutes of bitumen extraction was observed to reduce to about 44% at 25°C (Figure 4.9) as compared to about 91% at 50°C (Figure 4.3). Similarly, solids to bitumen ratio corresponding to 10-minute recovery were observed to be 0.2 at 25°C (Figure 4.10) as against 0.1 at 50°C (Figure 4.3). Hence for the base case, decreasing the operating temperature decreases both bitumen recovery as well as solids to bitumen ratio.

Figure 4.8 shows the bitumen recovery with respect to flotation time for kerosene soaked ore, soaked for 15 minutes and extraction done at 25°C. It shows that the maximum improvement occurred for 2 ml addition of kerosene. For 4 ml and 6ml addition the results were similar but net bitumen recovery for 20 minutes was lower than 2 ml addition case. Hence, a higher quantity of kerosene is not beneficial. Figure 4.9 indicates that for the base case, increasing the recovery time from 10 to 20 minutes led to increase in the bitumen recovery from around 44% to 80%. Figure 4.10 shows that bitumen froth recovered for 10 minutes for base case had almost double the solids to bitumen ratio as compared to 20 minutes recovery. However, it remained at same levels for the ores soaked in kerosene cases both for 10 minute and 20-minute recovery because of the very low quantity of solids in the froth.

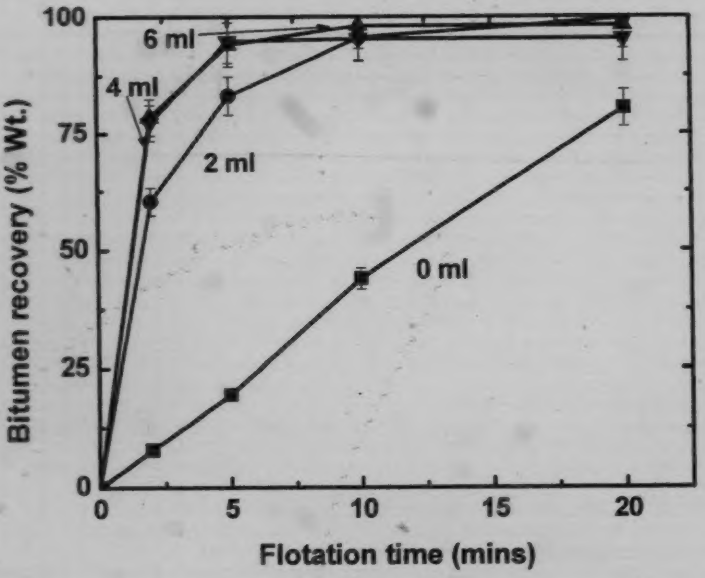


Figure 4.8: Bitumen recovery vis a vis flotation time for kerosene soaked in good processing ore for 15 minutes and extraction done at 25°C for 20 minutes recovery

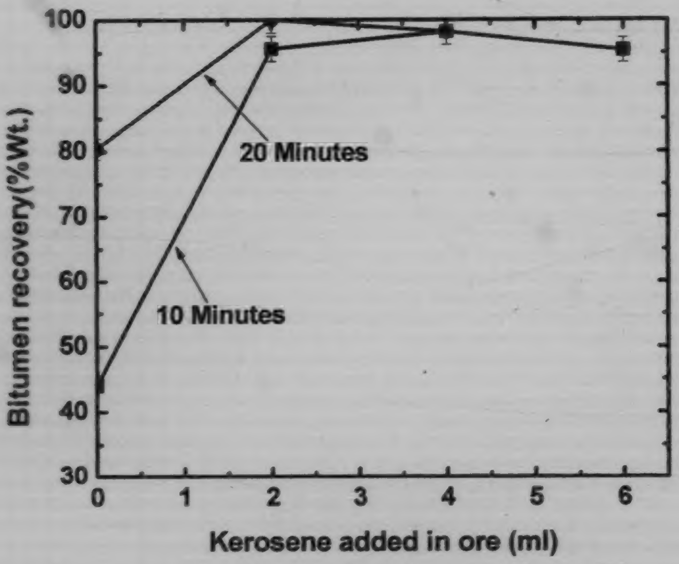


Figure 4.9: Bitumen recovery for kerosene soaked in good processing for 15 minutes and extraction done at 25°C for 10 minutes and 20 minutes recovery

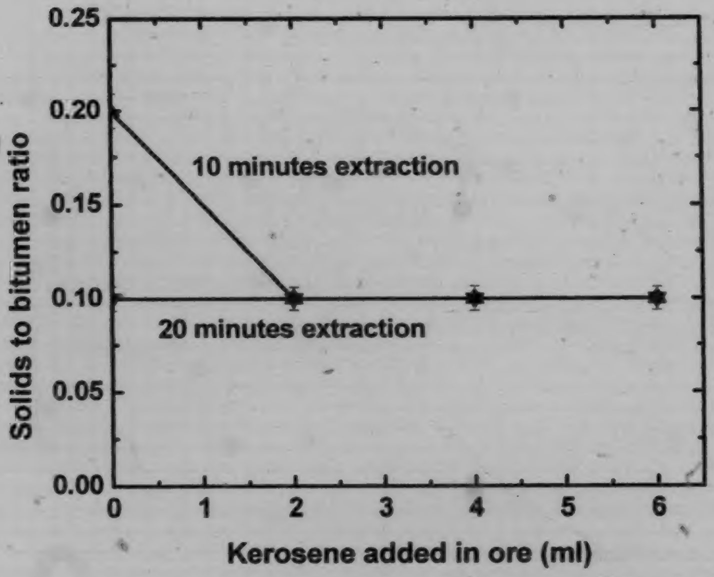


Figure 4.10: Solids to bitumen ratio for the froth of kerosene soaked in good processing ore for 15 minutes and extraction done at 25°C for 10 minutes and 20 minutes extraction

4.3.2 IMPACT ON POOR PROCESSING ORES

For poor processing ore-A for base case (without solvent addition) bitumen recovery corresponding to 10 minutes of bitumen extraction was observed to reduce to about 30% at 25°C (Figure 4.12) as compared to about 80% observed at 50°C (Figure 4.4). Figure 4.12 shows that by increasing the extraction time from 10 minutes to 20 minutes, the bitumen recovery was improved by about 10-15% for the base case as well as for the cases in which 2ml, 4ml, 6ml and 15 ml kerosene respectively was soaked in the ore. Similarly, Figure 4.13 shows that solids to bitumen ratio were lower for 20 minutes extraction as compared to 10-minute extraction at the addition levels of 0-6 ml kerosene in the ore. In view of the higher recovery and reduced solids to bitumen ratio for 20 minute recovery as compared to 10 minute recovery, all the experimental results for poor processing ore and weathered poor processing ores discussed in this section are based on both 10 minutes as well as 20 minutes of bitumen extraction.

4.3.2.1 EFFECT OF DIFFERENT SOAKING TIME PERIODS

In this section, results obtained for bitumen recovery and solids to bitumen ratio for kerosene soaking in poor processing ore-A for 5, 15 and 30 minutes have been discussed.

KEROSENE SOAKED IN ORE FOR 5 MINUTES: Experimental procedure described in 4.1.1 was used and kerosene soaking in the ore was carried out for 5 minutes. The results obtained for bitumen recovery variation with flotation time as well as bitumen recovery and solids to bitumen ratio variation with kerosene addition in the ore are shown in Figure 4.11, 4.12 and 4.13 respectively. Figure 4.11 and 4.12 shows that due to kerosene addition, bitumen recovery improved. The increase in bitumen recovery was sharp at lower levels of 2 - 4 ml and lessened at higher additions of 6-15 ml. Maximum improvement was observed for 6 ml addition and thereafter it stabilized for 15 ml addition. Figure 4.13 shows that solids to bitumen ratio increased upto 2 ml kerosene addition and decreased at higher addition of kerosene. The initial increase in the solids to bitumen ratio is due to increase in the quantity of froth generated due to kerosene addition in the ore. Higher solids to bitumen ratio at 0-2ml additions were due to higher incremental solids content as compared to bitumen quantity in the recovered forth. A 4-15 ml addition of kerosene led to higher incremental increase in bitumen recovery as compare to the solids in the bitumen froth leading to a decrease in solids to bitumen ratio.

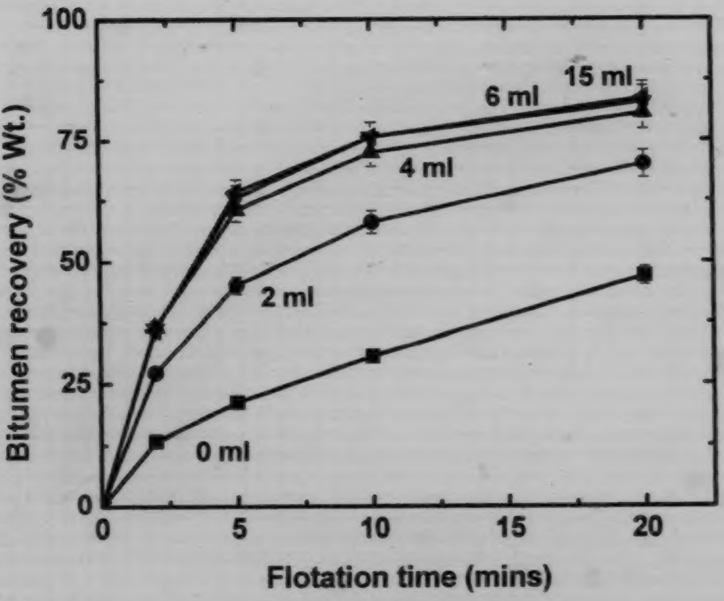


Figure 4.11: Bitumen recovery vis a vis flotation time for kerosene soaked in a poor processing ore-A for 5 minutes and extraction done at 25°C for 20 minutes recovery

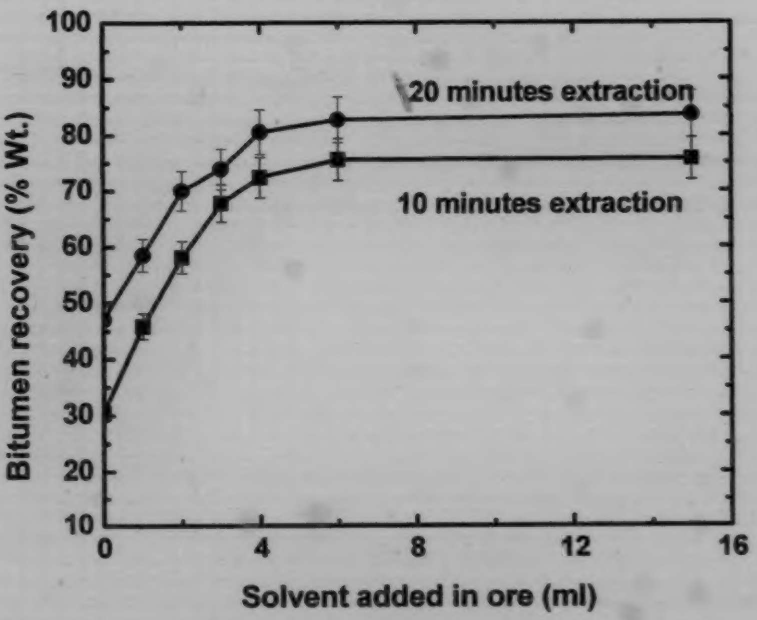


Figure 4.12: Bitumen recovery for kerosene soaked in a poor processing ore-A for 5 minutes and extraction done at 25°C for 10 and 20 minutes recovery

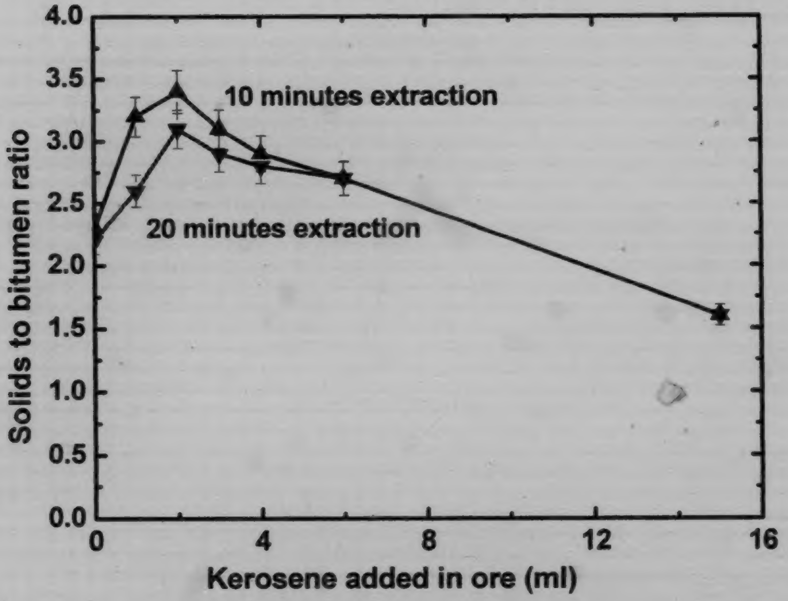


Figure 4.13: Solids to bitumen ratio for kerosene soaked in a poor processing ore-A for 5 minutes and extraction done at 25°C for 10 and 20 minutes recovery

KEROSENE SOAKED IN ORE FOR 15 MINUTES: The results for bitumen recovery obtained for kerosene soaked in ore for 15 minutes are similar to those observed for 5 minutes of soaking time but the improvement is relatively less as compared to 5 minutes case (Refer table – A.19 and A.21 for the bitumen recovery for two cases). Figure 4.14 shows bitumen recovery variation with flotation time. For 2 ml and 4 ml addition levels, the trend is similar to what was observed for 5 minutes soaking case but for 6 and 15 ml cases, there is a slight deterioration. Figure 4.15 shows that with the addition of kerosene, bitumen recovery improved and maximum improvement was observed for 4 ml addition and thereafter decreased at higher addition of kerosene of 6-15 ml. This observation is similar to what was observed for 5 minutes of ore soaking case.

The decrease in the recovery at and after 6 ml addition of kerosene indicates that the incremental increase in the bitumen recovery is less than the incremental addition of kerosene added for ore soaking for 15 minutes. As against this, in the 5 minutes case, the incremental increase in bitumen recovery equaled the incremental kerosene addition and bitumen recovery at 15 ml addition was same as was observed at 6 ml addition (Figure 4.12). Figure 4.16 shows the results for solids to bitumen ratio, which increased initially at 1-2 ml kerosene addition and then decreased with higher addition similar to 5 minutes soaking case.

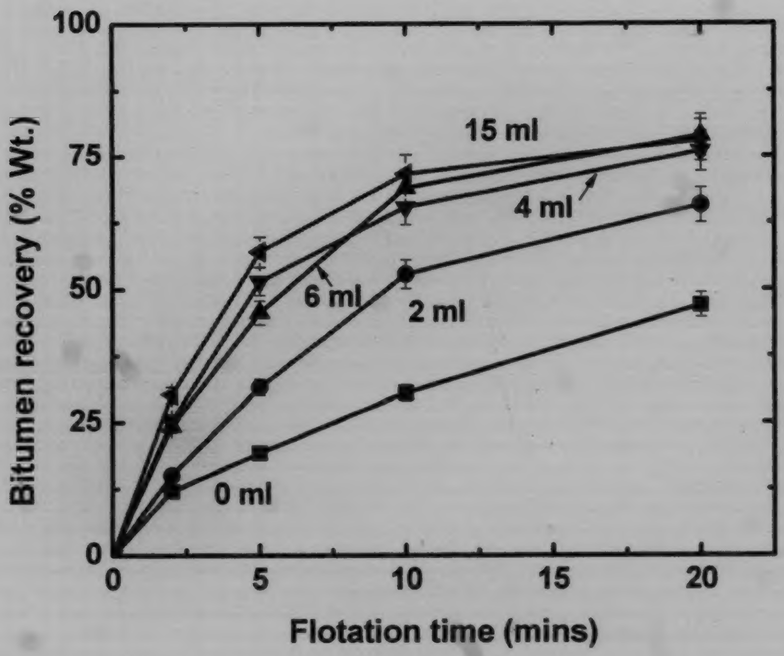


Figure 4.14: Bitumen recovery vis a vis flotation time for kerosene soaked in a poor processing ore-A for 15 minutes and extraction done at 25°C for 20 minutes recovery

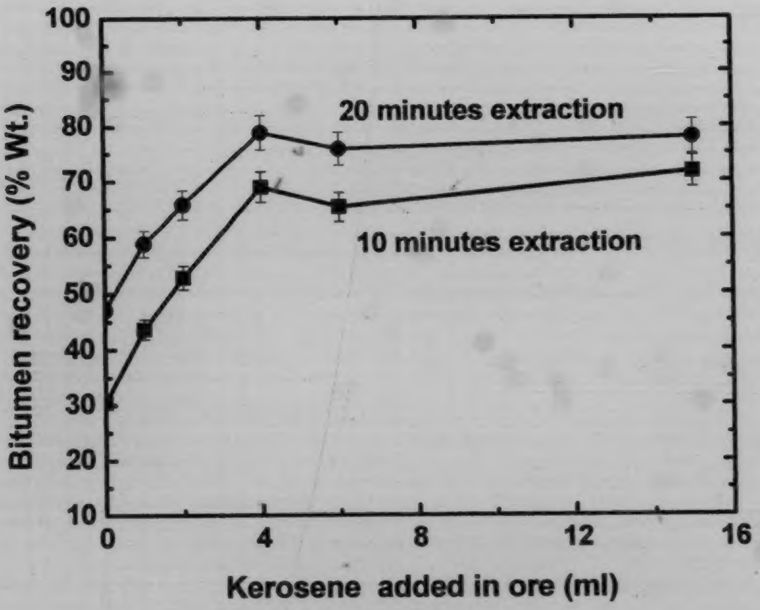


Figure 4.15: Bitumen recovery for kerosene soaked in a poor processing ore-A for 15 minutes and extraction done at 25°C for 10 and 20 minutes recovery

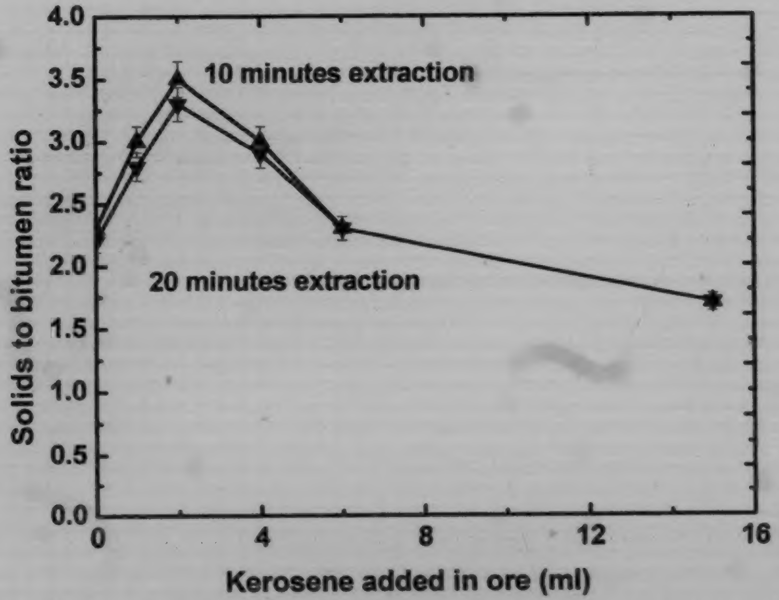


Figure 4.16: Solids to bitumen ratio for kerosene soaked in a poor processing ore-A for 15 minutes and extraction done at 25°C for 10 and 20 minutes recovery

KEROSENE SOAKED IN ORE FOR 30 MINUTES: The results obtained for ore soaking in kerosene for 30 minutes show further deterioration as compared to 5 and 15 minute soaking cases. Figures 4.17 and 4.18 indicates that bitumen recovery improved upto 4 ml addition of kerosene to same levels as observed in 5 and 15 minute cases but decreased thereafter at higher addition of kerosene of 6-15 ml. The solids to bitumen ratio of Figure 4.19 however, show an entirely different pattern. It increased even at higher dosage of kerosene as against previous cases in which it increased initially and then decreased at 6- 15 ml of kerosene addition. This result shows that higher soaking period for poor processing ore is not beneficial for reduction in solids to bitumen ratio in the froth.

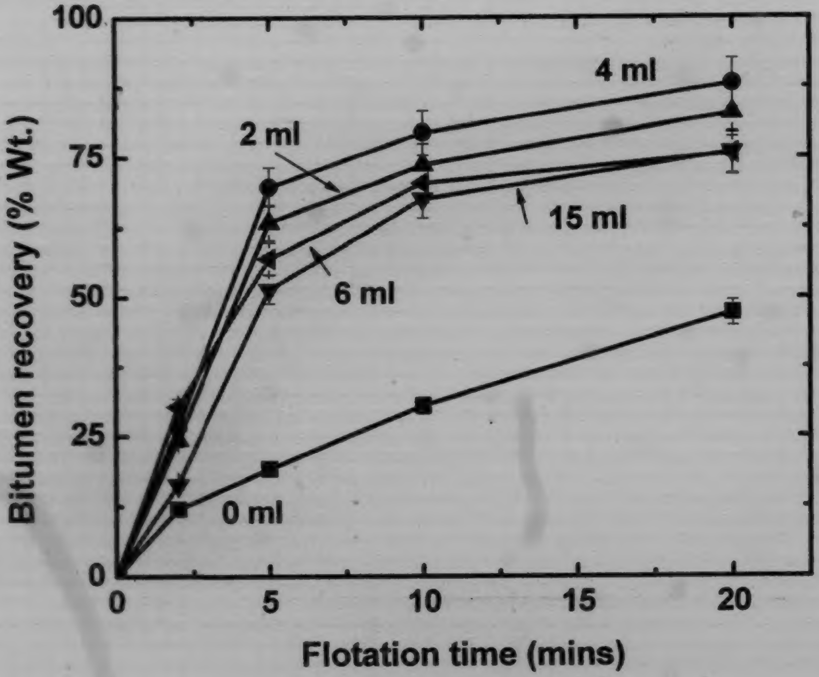


Figure 4.17: Bitumen recovery with respect to flotation time for kerosene soaked in a poor processing ore-A for 30 minutes and extraction done at 25°C for 20 minutes recovery

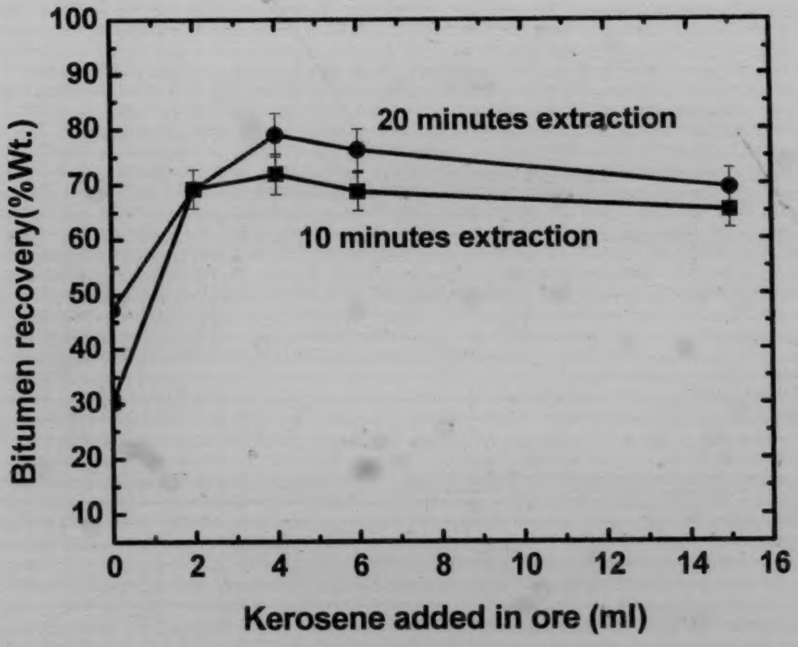


Figure 4.18: Bitumen recovery for kerosene soaked in a poor processing ore-A for 30 minutes and extraction done at 25°C for 10 and 20 minutes recovery

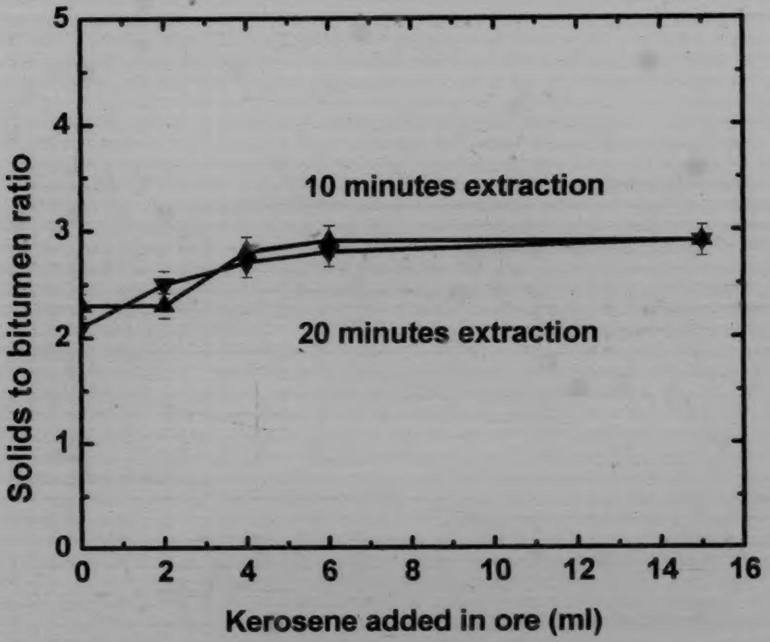


Figure 4.19: Solids to bitumen ratio for kerosene soaked in a poor processing ore-A for 30 minutes and extraction done at 25°C for 10 and 20 minutes recovery

4.3.3 IMPACT ON WEATHERED POOR PROCESSING ORES

The poor processing ore-A was weathered artificially in an oven at 50°C under airflow for 1-week. This weathered poor processing ore was soaked in kerosene for 15 minutes and the results obtained for various levels of kerosene addition are discussed below. Figure 4.21 shows that 20 minutes bitumen recovery for weathered poor processing ore reduced to less than 10 % as compared to about 48% for the same poor processing ore A (Figure 4.15). Figure 4.20 shows that the low dosages of kerosene addition improved the bitumen recovery but higher quantities of the order of 15 ml kerosene addition only improved the recovery considerably for the weathered ore. This is in contrast to the observation for poor processing ore A where 2-4 ml kerosene addition increased the bitumen recovery to maximum levels (Figure 4.14) and higher levels of kerosene addition had not much effect on further improvement in bitumen recovery. However, even at 15 ml addition level, the bitumen recovery could improve to about 60% only for the weathered ore. Solids to Bitumen ratio in the case of weathered poor processing ore (when no solvent was added) increased from about 2.2 (Figure 4.16) to about 8.7 (Figure 4.22) simply on account of weathering. Figure 4.22 shows that solids to bitumen ratio decreased continuously for kerosene soaked ores. This trend is different from the observation for poor processing ore soaked in kerosene for similar case (Figure 4.16) where it increased initially upto 1-2 ml kerosene addition levels and then decreased with higher addition of kerosene in the ore. These observations show that the loss in bitumen recovery and increase in solids to bitumen ratio due to weathering of the poor processing ore can also be improved by using kerosene but very high quantities of solvent are required for desired levels of recovery and solids to bitumen ratio.

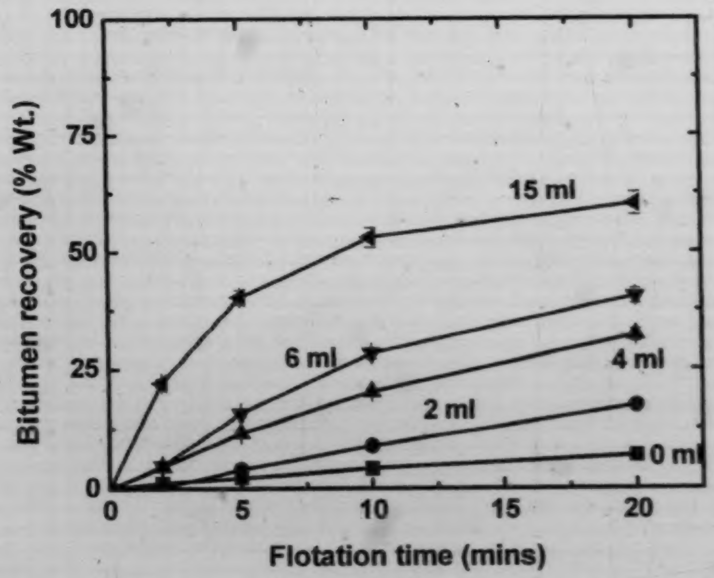


Figure 4.20: Bitumen recovery vis a vis flotation time for kerosene soaked in weathered poor processing ore-C for 15 minutes and extraction done at 25°C for 20 minutes

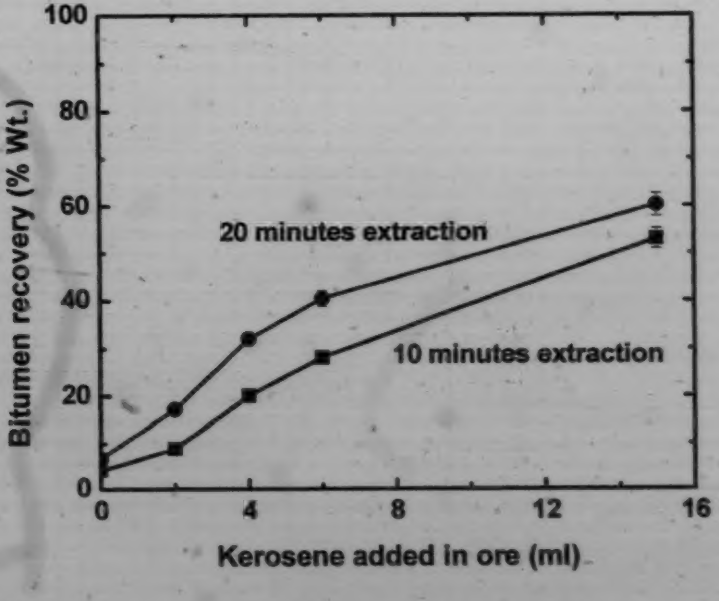


Figure 4.21: Bitumen recovery for kerosene soaked in weathered poor processing ore-C for 15 minutes and extraction done at 25°C for10 and 20 minutes

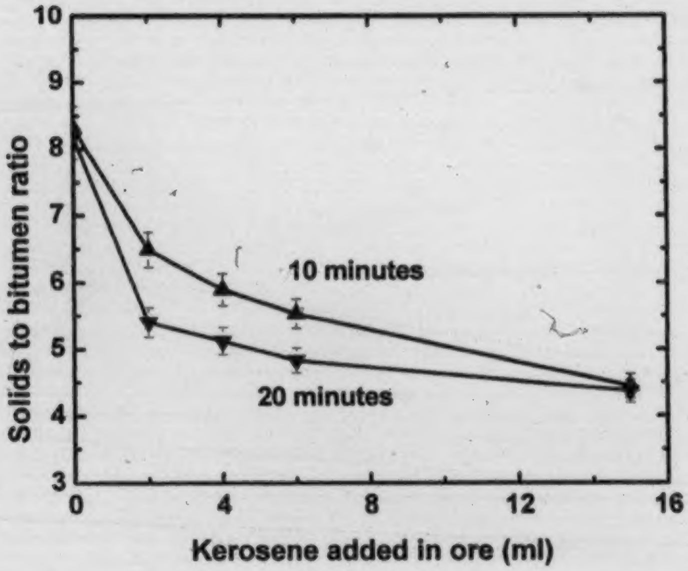


Figure 4.22: Solids to bitumen ratio for kerosene soaked in weathered poor processing ore-C for 15 minutes and extraction done at 25°C for 10 and 20 minutes

4.4 PARTICLE SIZE DISTRIBUTION OF SOLIDS IN RECOVERED BITUMEN FROTH

The solids recovered in the froth for various cases of ore soaked in kerosene were further analyzed for particle size distribution. This was carried out to observe the impact of ore soaking in kerosene on changes in % wt. fines in the solids recovered at various levels of kerosene addition. The solids recovered in kerosene soaked ore froth for various cases were analyzed for % wt. fines using procedure described in section 3.3.1. Comparison of % wt. fines has been carried out for two different cases. First, is the comparison of fines in kerosene soaked poor processing ore-A (15 minutes soaking) extracted froths at 50°C and 25°C. Second, is the comparison of the fines in the solids recovered for kerosene soaked good processing ore, poor processing ore and weathered poor processing ore extracted at 25°C (15 minutes soaking).

4.4.1 IMPACT AT 50°C vis. a vis. 25°C EXTRACTION

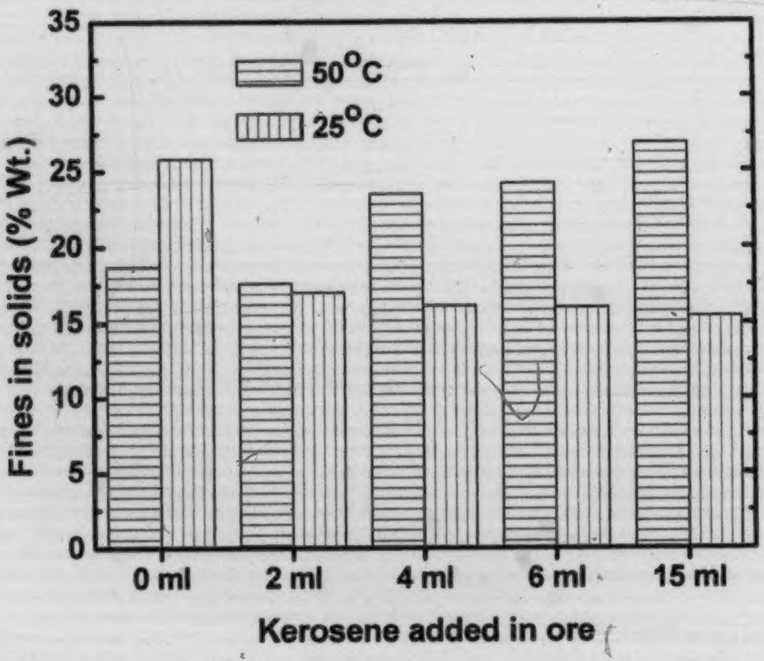


Figure 4.23: Percent fines in the solids for the froth from kerosene soaked in poor processing ore for 5 minute and extraction done at 25°C and 50°C for 20 minutes froth recovery

Figure 4.23 shows that at 50°C extraction, the reduction in the total solids in the recovered froth due to ore soaking in kerosene is contributed by the increase in the % wt. fines in the solids i.e. % wt. of coarser particles decreases and fines increases with the addition of kerosene in the ore. However at 25°C extraction, the reduction in the total solids in the recovered froth is attributed by decrease in the % wt. fines in the solids with the addition of kerosene. Another observation is that at 25°C maximum reduction in solids as well as % wt. fines in the solids is observed at initial 2 ml addition and the decrease is gradual at higher quantities of kerosene in the ore.

4.4.2 IMPACT ON DIFFERENT TYPES OF ORES AT 25°C EXTRACTION

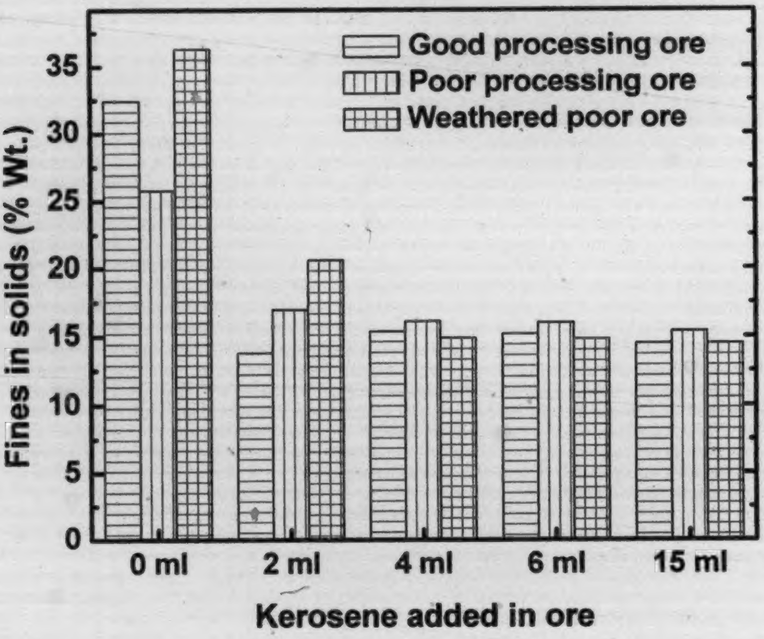


Figure 4.24: Percent fines in the solids for the froth from kerosene soaking in different oil sand ores for 15 minutes and extraction done at 25°C for 20 minutes froth recovery

The results of % wt. fines determination in the solids recovered for kerosene soaked good processing ore, poor processing ore and weathered poor processing ore extracted at 25°C showed similar trends. The reduction in the total solids in the recovered froth for all the three types of ores is contributed by the decrease in the % wt. fines in the solids with maximum reduction in % wt. fines in the solids occurring at initial 2 ml addition of kerosene to the ore. These observations for % wt. fines in kerosene soaked ore at 50°C and 25°C are in line with the similar observation for the % wt. fines in the solids from naphtha spray washed froth of poor processing ore generated at 35°C and 50°C discussed in section 3.3.2.

4.5 KEROSENE LOSS TO TAILINGS WATER

Use of a solvent for enhancing bitumen recovery would require analysis of the distribution of the solvent during the extraction process. It is required to determine the distribution of the solvent added to the ore in the recovered bitumen froth, tailings water and its potential association with the solids in the tailing water. In this set of experiments, a study has been conducted to estimate the loss of kerosene in the tailings water. The loss of the kerosene quantity into the tailings water is estimated as a wt. % on the initial added solvent to the ore.

4.5.1 EXPERIMENTAL PROCEDURE

The following steps were used for obtaining the tailings water sample for further analysis for the kerosene presence:

- The tailings generated during the bitumen extraction from kerosene soaked ore using Denver cell and procedure discussed in section 4.1.1 were carefully transferred into two 500 ml PPCO (Polypropylene copolymer) centrifuge bottles.
- These bottles were centrifuged at 33 rev/s for 20 minutes to separate the solid particles from the tailings water.
- After centrifuging, the solids free tailings water was carefully transferred into two 250 ml glass bottles ensuring that no settled solids get entrained along with the clear

tailings water. These tailings water samples were sent for its further analysis by an external agency.

- For this study, two sets of experiments were carried out for tailings water samples, which were tested for kerosene loss into the tailings water. One set of tailings water sample each at 50°C and 25°C extraction for poor processing ore-A soaked in kerosene for 15 minutes corresponding to 0 ml, 4ml and 15 ml addition level respectively.

4.5.2 TAILINGS WATER ANALYSIS

The kerosene loss into the tailings water was analyzed using the water samples prepared following the procedure detailed in section 4.5.1. These samples were analyzed by an external agency, Maxxam Analytics, Edmonton Environmental. The analysis discussed in this section is based on the report submitted by Maxxam Analytics, which is enclosed as Appendix E. The analysis is based upon chromatogram analysis of water samples for the carbon content observed in the tailings water in which ore soaked in kerosene was used and comparing it with the base case in which no solvent was added.

Kerosene comprises carbon chains from C10-C20. Any amount of kerosene quantity from the ore soaked in kerosene lost to the tailings water during extraction process can be checked by the increase in the C10-C20 content in this tailings water and comparing to the base case where no kerosene was added. The concentration of C10-C20 in mg/L present in the tailings water is estimated using the relative area count of the C10-C20 for each sample from the chromatogram report. The estimates include all the components that feature C10 through to C20. The best way to check kerosene in the tailings water sample is by subtracting the C10-C20 component of the base case from the

C10-C20 component in the sample. This approach was used based on the assumption that with all other operating conditions remaining the same, any increase in the C10-C20 area count and hence its concentration in the tailings water would be due to the addition of kerosene in the ore.

4.5.3 RESULTS AND DISCUSSION

Tables 4.3 and 4.4 show the C10-C20 count estimated for tailings water from kerosene soaked poor processing ore at 50°C and 25°C, respectively.

Table 4.3: Estimated carbon count in tailings water from kerosene soaked poor processing ore at 50°C (As reported in tailings water analysis from Maxxam analytics)

Kerosene added in the ore **Tailings water composition**	**ml**	**0.0**	**4.0**	**15.0**
C10-C20	mg/L	3.7	4.9	40.7
C10-C30 Total Extractables	mg/L	4.6	6.3	53.2
C20-C30 (By difference)	mg/L	0.9	1.4	12.5

Table 4.4: Estimated carbon count in tailings water from kerosene soaked poor processing ore at 25°C (As reported in tailings water analysis from Maxxam analytics)

Kerosene added in the ore **Tailings water composition**	**ml**	**0.0**	**4.0**	**15.0**
C10-C20	mg/L	1.6	3.1	18.6
Total Extractables C10-C30	mg/L	3.6	4.1	23.8
C20-C30 (By difference)	mg/L	2.0	1.0	5.2

The amount of loss of kerosene in the tailings water has been calculated using the following basis:

- Only carbon and hydrogen molecules constitute the kerosene compound
- Carbon / hydrogen ratio is 0.49 in kerosene (wt.%)
- Additional carbon count C-10 to C-20 estimated in the tailings water from the kerosene soaked ore are from kerosene added in the ore

Using the data given in Tables 4.3 and 4.4, the amount of kerosene loss in the tailings water as a function of the amount added in the ore in respective cases has been calculated.

Table 4.5: Kerosene loss in tailings water as % wt. on kerosene added in ore at 50°C

Kerosene added in ore	**ml**	**0**	**4**	**15**
Kerosene added in ore **(Z)***	mg	0.0	3200.0	12000.0
Carbon (C10-C20) in tailings water **(A) #**	mg/L	3.7	4.9	40.7
Hydrogen in tailings water (@ C/H 0.49) **(B=A/0.49)**	mg/L	7.6	10.0	83.1
Kerosene in tailings water **(A+B)**	mg/L	11.3	14.9	123.8
Additional kerosene as compared to 0 ml case **(X)**	mg/L		3.6 @	112.5
Total kerosene in 0.85 liter of tailings water **(Y= X*0.85)**	mg		3.1	95.6
% Kerosene loss in tailings water **(Y/Z*100)**	%		**0.1**	**0.8**

* Using 800 kg/m^3 density of kerosene
# From Table 4.3
@ 14.9-11.3 from previous row

\Table 4.6: Kerosene loss in tailings water as % wt. on kerosene added in ore at 25°C

Kerosene added in ore	**ml**	**0**	**4**	**15**
Kerosene added in ore **(Z)***	mg	0.0	3200.0	12000.0
Carbon (C10-C20) in tailings water **(A)** #	mg/L	1.6	3.1	18.6
Hydrogen in tailings water (@ C/H 0.49) **(B=A/0.49)**	mg/L	3.3	6.3	38.0
Kerosene in tailings water **(A+B)**	mg/L	4.9	9.4	56.6
Additional kerosene as compared to 0 ml case **(X)**	mg/L		4.5	51.7
Total kerosene in 0.85 liter of tailings water **(Y= X*0.85)**	mg	0.0	3.9	43.9
% Kerosene loss in tailings water **(Y/Z*100)**	%		**0.1**	**0.4**

* Using 800 kg/m^3 density of kerosene
# From Table 4.3
@ 9.4-4.9 from previous row

From Tables 4.5 and 4.6 it is noted that the kerosene loss in tailings water is low at 25°C extraction as compared to that observed at 50°C. For 4 ml addition of kerosene in the poor processing ore, the losses in the tailings is only 0.1% of the initial quantity added in the ore. However, for 15 ml kerosene addition in the ore, the kerosene loss is around 1.0 % and 0.4 % at 50°C and 25°C, respectively. For the purpose of this study, the losses of kerosene to the tailings water has been neglected assuming that the amount of kerosene added in the respective cases has been recovered along with the bitumen froth. Hence the amount of kerosene added to the ore in all the experimental results has been subtracted from the actual results of bitumen recovery in a froth to represent the net bitumen recovery improvement.

4.6 ANALYSIS OF BITUMEN FROTH MORPHOLOGY

4.6.1 CONFOCAL LASER SCANNING MICROSCOPY

The Confocal Laser Scanning Microscopy (CLSM) technique uses some features of Light Microscopy (LM) and Scanning Electron Microscopy (SEM), to scan and image the bitumen froth sample point-by-point with a finely focused laser beam. The confocal microscope used for this set of experiments is a spinning disc confocal microscope from Quorum Technologies, Inc. The froth samples were imaged immediately after (10-15 minutes) the fresh froth samples were collected. Froth was placed between two glass cover slips (hydrophobic surface) to reduce water movement. The bitumen froth sample images were taken using CLSM which has an option of sequential acquisition of images in two wavelengths by exciting the bitumen component using 491 nm blue light laser and detecting the fluorescence image in the green region at 528 nm. The representative image of a froth sample was a result of stacking of images obtained at different height sections of the froth samples.

4.6.2 SAMPLE PREPARATION AND ORES USED

A fresh bitumen froth samples were produced using procedure described in section 4.1.1. Investigation has been carried out to analyze the microscopic images of bitumen froth obtained from good processing ore, poor processing ore as well as weathered poor ore for following different cases:

- Good processing ore bitumen froth generated at 50°C without kerosene addition in the ore.
- Good processing ore bitumen froth generated at 25°C for 0 ml, 4 ml and 15 ml kerosene addition.
- Poor processing ore bitumen froth generated at 50°C for 0 ml and 4 ml kerosene addition.
- Poor processing ore bitumen froth generated at 25°C for 0 ml, 4 ml and 15 ml kerosene addition.
- Weathered poor processing ore (Artificially weathered in an oven at 50°C under air flow for 1 week) bitumen froth generated at 25°C for 0 ml, 4 ml and 15 ml kerosene addition.

4.6.3 CONFOCAL MICROSCOPIC IMAGES OF BITUMEN FROTHS

The microscopic images obtained for bitumen froth morphologies for the different cases are represented in Figures 4.25 to 4.36. Each figure represents four different images of the same sample taken at different locations. The observations for these images are discussed below

4.6.3.1 GOOD ORE FROTH AT 50°C EXTRACTION WITHOUT KEROSENE ADDITION

Figure 4.25 shows the image of a bitumen froth generated at 50°C for the good processing ore without kerosene addition in the ore. The bitumen shown in the images obtained for this case is featureless which is an attribute to "normal" bitumen. The dark circular spots in the image correspond to water droplets and the variation in the fluorescence can be attributed to the differences in chemical composition.

4.6.3.2 GOOD ORE FROTH AT 25°C EXTRACTION WITH AND WITHOUT KEROSENE ADDITION

Figures 4.26-4.28 represent the images of bitumen froth generated at 25°C for good processing ore for 0ml, 4ml and 15 ml kerosene addition in the ore, respectively. The bitumen froth shown in the images in these cases is also featureless and are similar to what was observed for the 50°C case. The featureless attribute of the normal bitumen at 25°C signifies that the morphology of bitumen froth for good processing ore did not change much for low operation temperature and the addition of kerosene to the ore also did not bring about any appreciable changes. However, the dark circular spots are observed to have reduced and are smaller in size for the kerosene soaked ore cases shown in Figures 4.27 and 4.28.

4.6.3.3 POOR ORE FROTH AT 50°C EXTRACTION WITH AND WITHOUT KEROSENE ADDITION

Figures 4.29 and 4.30 represent the images of bitumen froth generated at 50°C for the poor processing ore for 0ml and 4 ml kerosene addition in the ore respectively. Figure 4.29 shows an image that is quite different from the good processing ore froth images. The image shows various characteristic dark structures among the featureless phase of better fluorescence that represents normal bitumen. It is understood from the study done by Munoz et al. (2003) that these structures represent the presence of low or degraded quality bitumen in the froth. However, the image shown in Figure 4.30 for 4 ml kerosene soaked case shows that the characteristic structures are reduced considerably and these phases look quite similar to the better fluorescence continuous phases observed for good processing ore froth at 25°C and 50°C, although some structures are still observed.

4.6.3.4 POOR ORE FROTH AT 25°C EXTRACTION WITH AND WITHOUT KEROSENE ADDITION

Figures 4.31-4.33 represent the images of bitumen froth generated at 25°C for poor processing ore for 0 ml, 4 ml and 15 ml kerosene addition in the ore, respectively. Figure 4.31, corresponding to 0 ml kerosene addition case shows increased level of characteristic structures throughout the image. Also there are discontinuous and scattered spans of featureless regions. According to Munoz et. al (2003), these type of structures are understood to represent the low or degraded quality bitumen in the froth recovered at 25°C. However, as observed at 50°C, the images shown in Figures 4.32 and 4.33 for 4 ml and 15 ml kerosene soaked cases respectively shows larger spans of continuous phase of better fluorescence representing "normal" bitumen. Figure 4.33 represents the image, which look quite similar to the better fluorescence continuous region observed for good processing ore froth at 25°C and 50°C. The very fact that with solvent addition, the structure disappears would mean that solids have something to do with these structures.

4.6.3.5 WEATHRED POOR FROTH AT 25°C EXTRACTION WITH AND WITHOUT KEROSENE ADDITION

Figures 4.34-4.36 represent the images of bitumen froth generated at 25°C for artificially weathered poor processing ore for 0ml, 4 ml and 15 ml kerosene addition, respectively. Figure 4.34, corresponding to 0 ml kerosene addition case shows complex characteristic structures of various sizes and shapes throughout the image. There are negligible spans of featureless regions of better fluorescence. The images are understood to represent more degraded quality of bitumen in the froth recovered at 25°C.

The visual studies lead to an observation that weathering of the ore not only decreases the separation efficiency of solids from the oil sands and lower bitumen recovery but also possibly contributes to the highly degraded quality bitumen recovered in the forth. However, as observed for poor processing ore at 25°C and 50°C, the images shown in Figure 4.35 and 4.36 for 4 ml and 15 ml kerosene soaked cases, respectively shows larger spans of continuous phase of better fluorescence although these regions still have structures scattered within the image.

4.7 PHYSICAL PROPERTY MEASUREMENTS

In order to observe whether addition of kerosene to the ore cause any change in the characteristics of the solids recovered in the froth or tailings water quality, following property measurements were carried out:

- Zeta potential measurements for the fines in the solids recovered in the bitumen froth for various cases.
- Surface tension measurement for the solid free tailings water.

The details of the measurements carried out for various cases are given in Appendix E. No observable variation was observed in the zeta potential for the fines from the solids recovered in the froth as well as the surface tension for the solids free tailings water both at 50°C and 25°C for different types of ores.

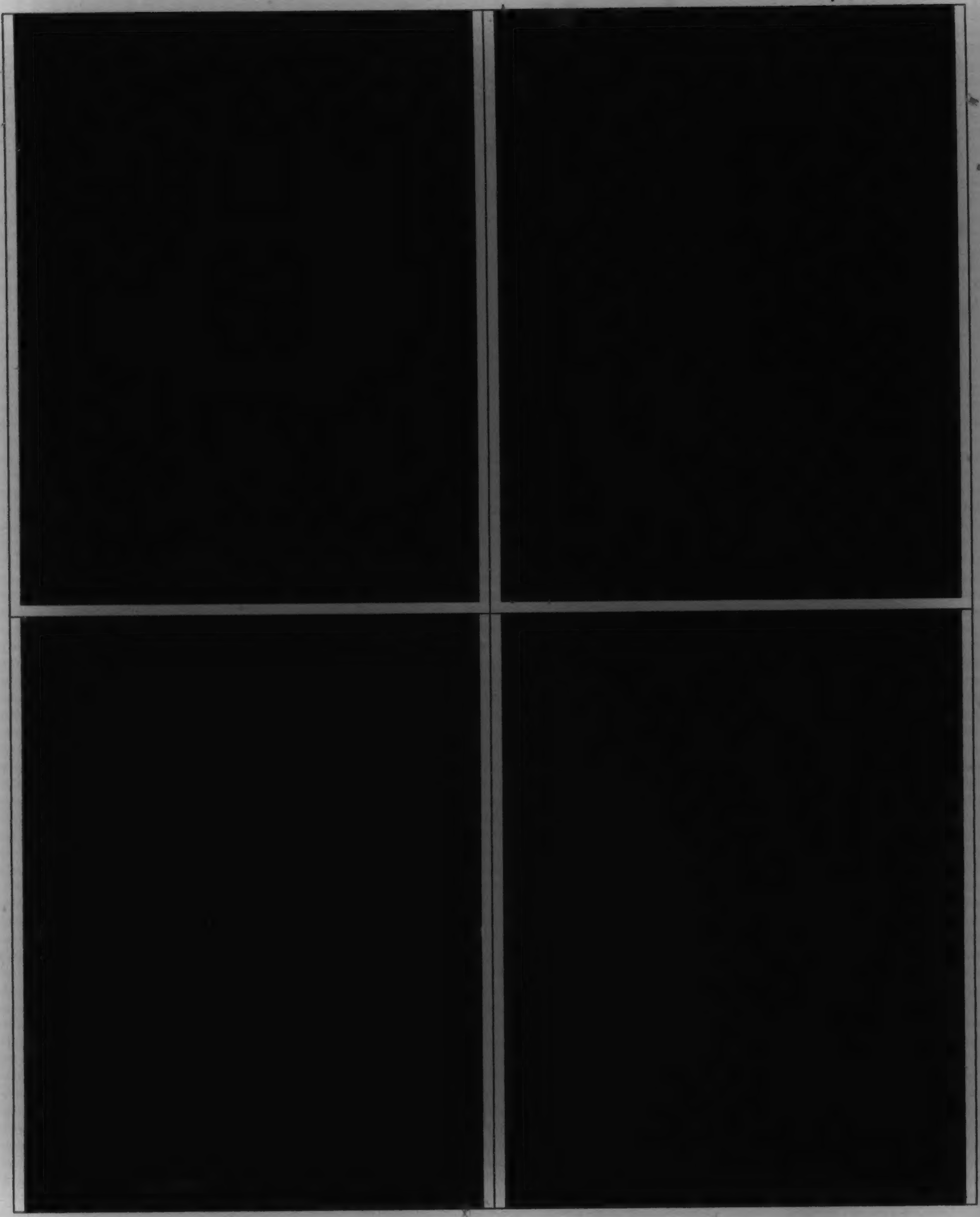


Fig 4.25: Microscopic analysis of froth from good ore with no solvent addition at 50^{o}C

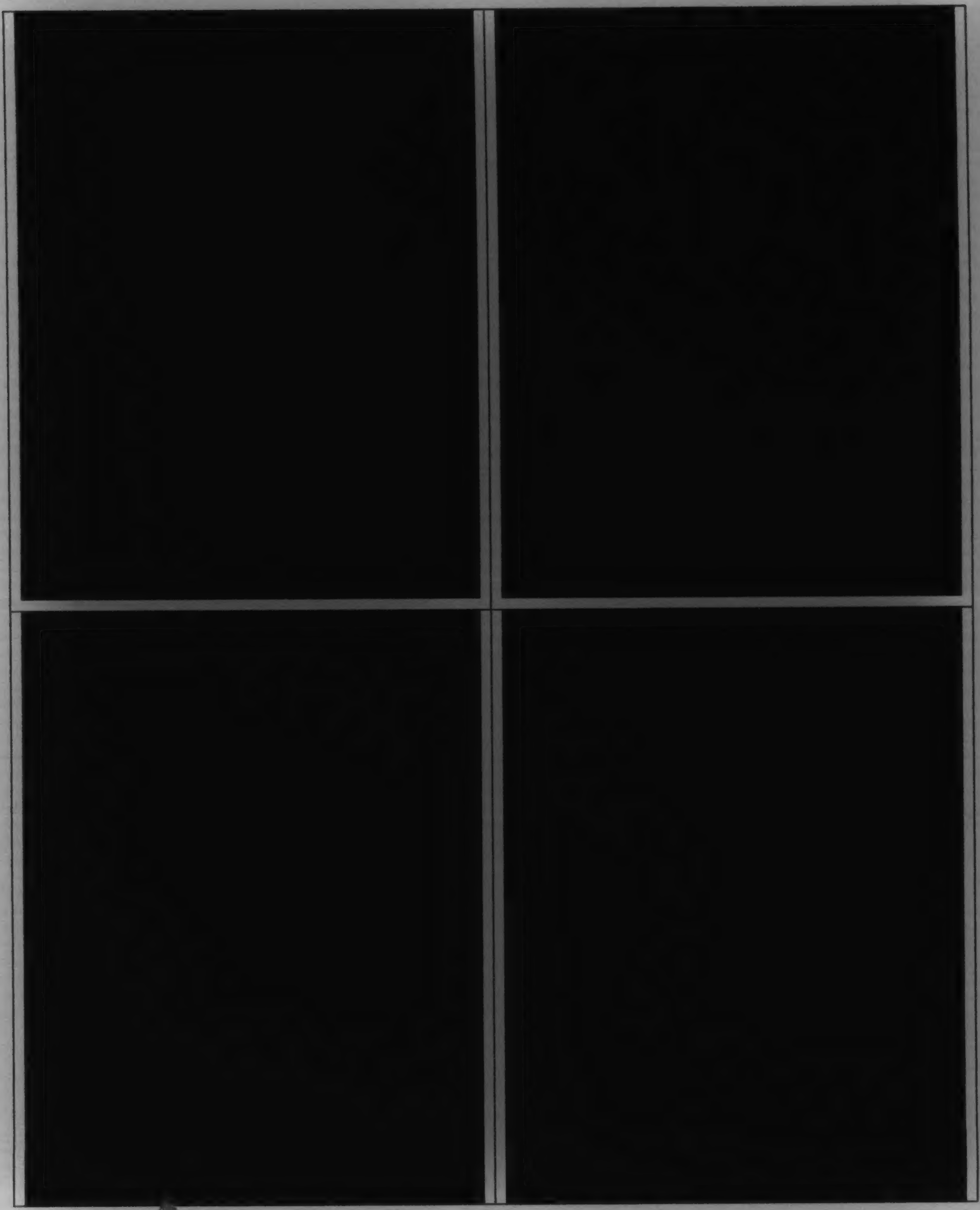


Fig 4.26: Microscopic analysis of froth from good ore with no solvent addition at 25°C

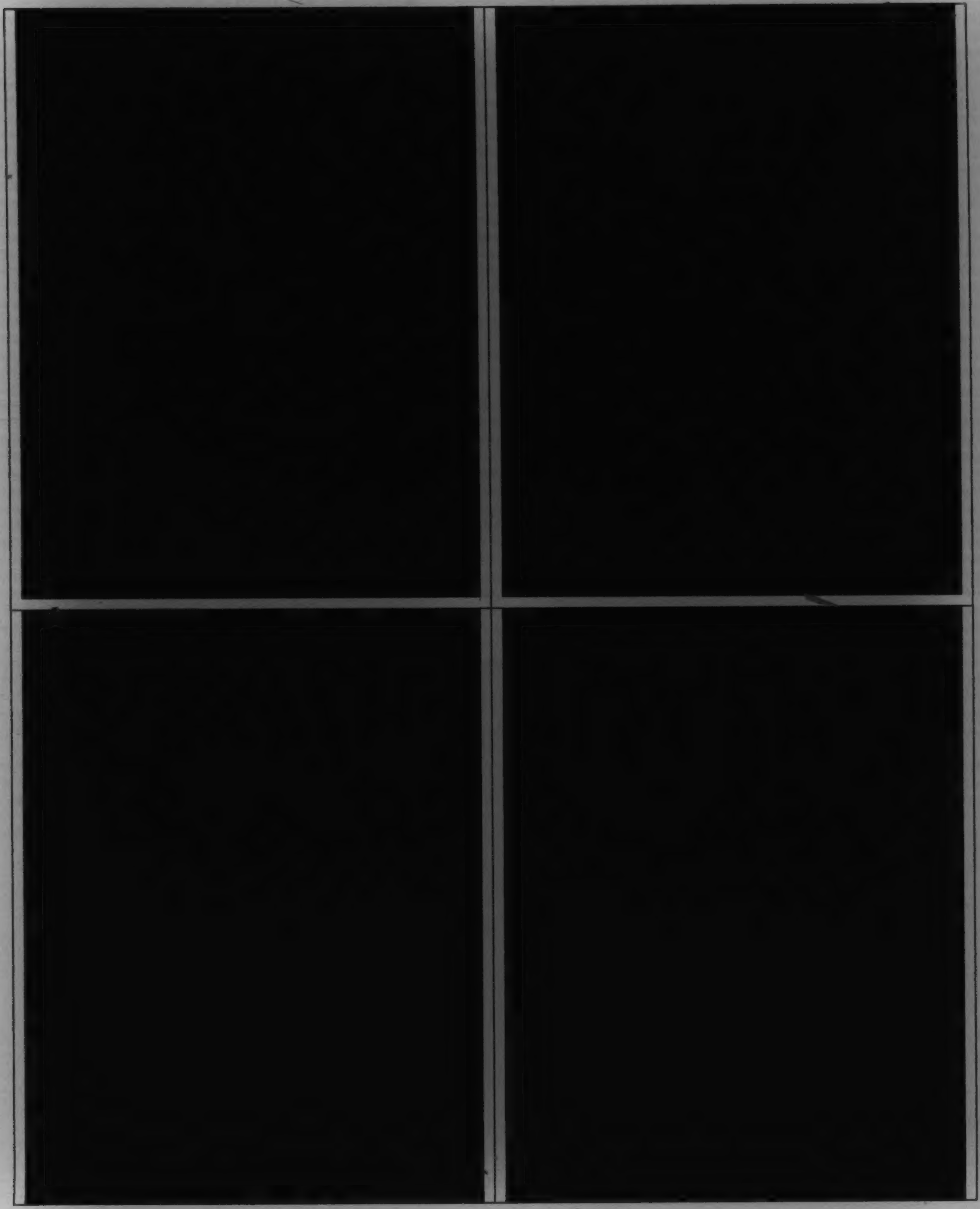


Fig 4.27: Microscopic analysis of froth from good ore with 4 ml kerosene at 25°C

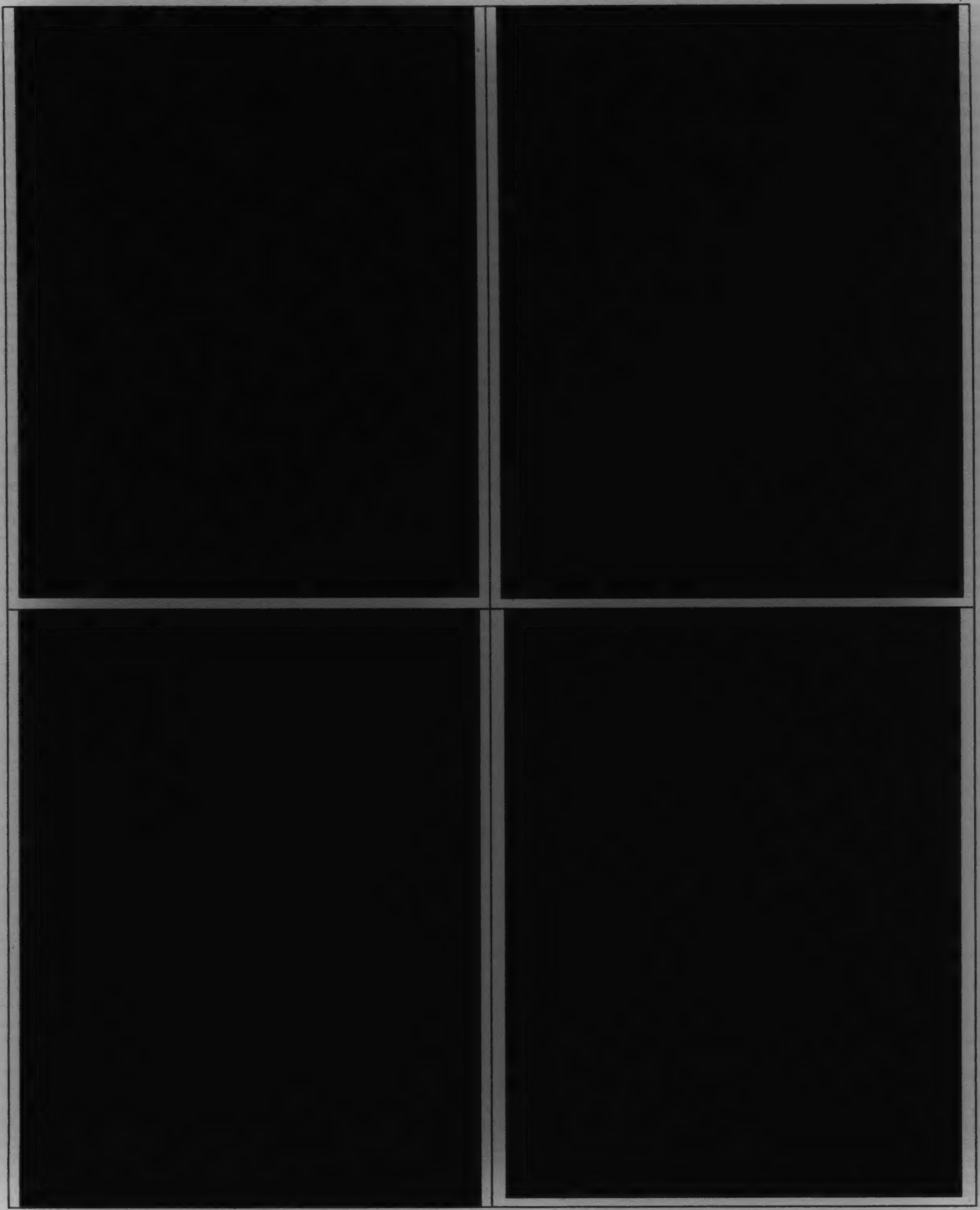


Fig 4.28: Microscopic analysis of froth from good ore with 15 ml kerosene at 25°C

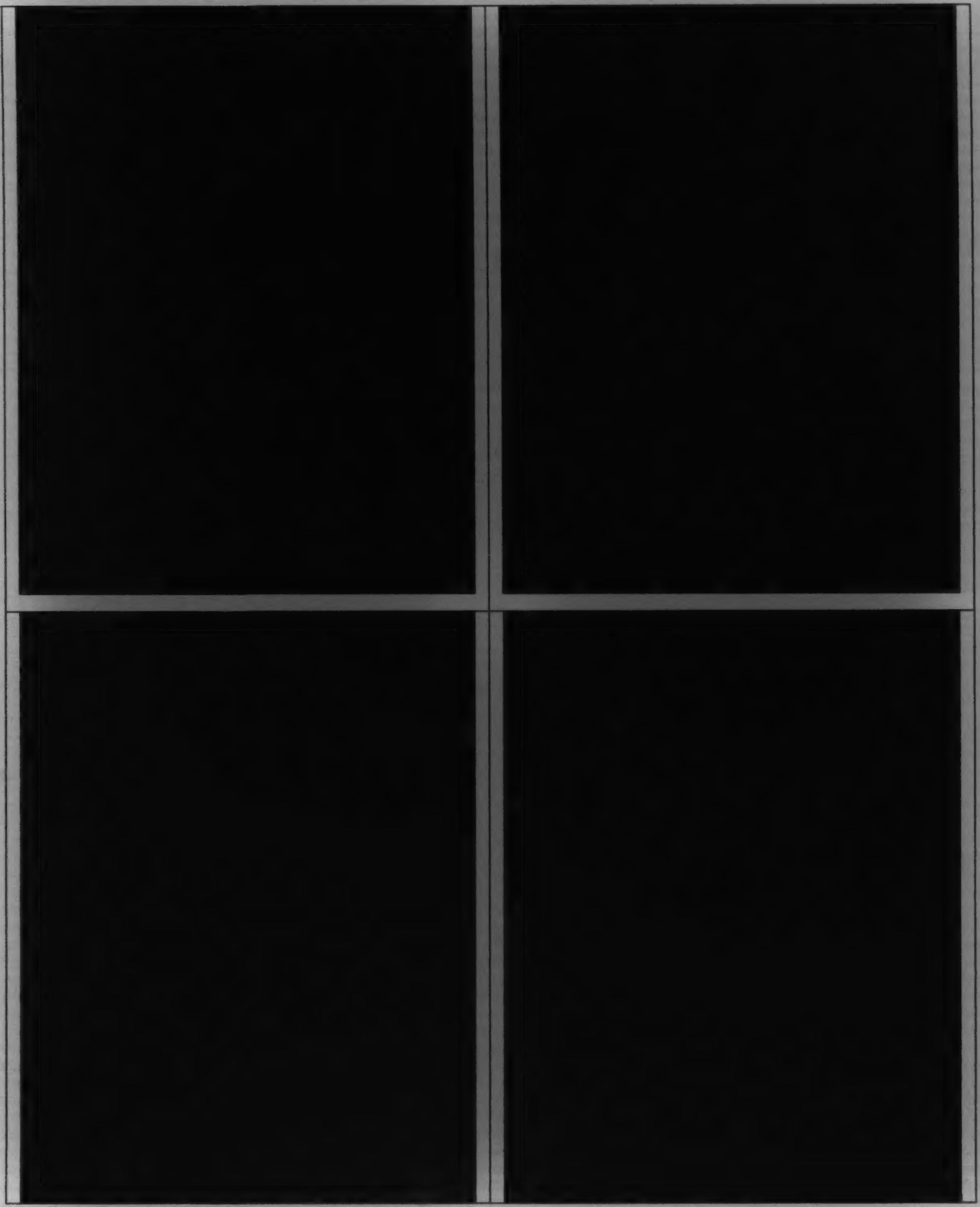


Fig 4.29: Microscopic analysis of froth from poor ore with 0 ml kerosene at 50^{o}C

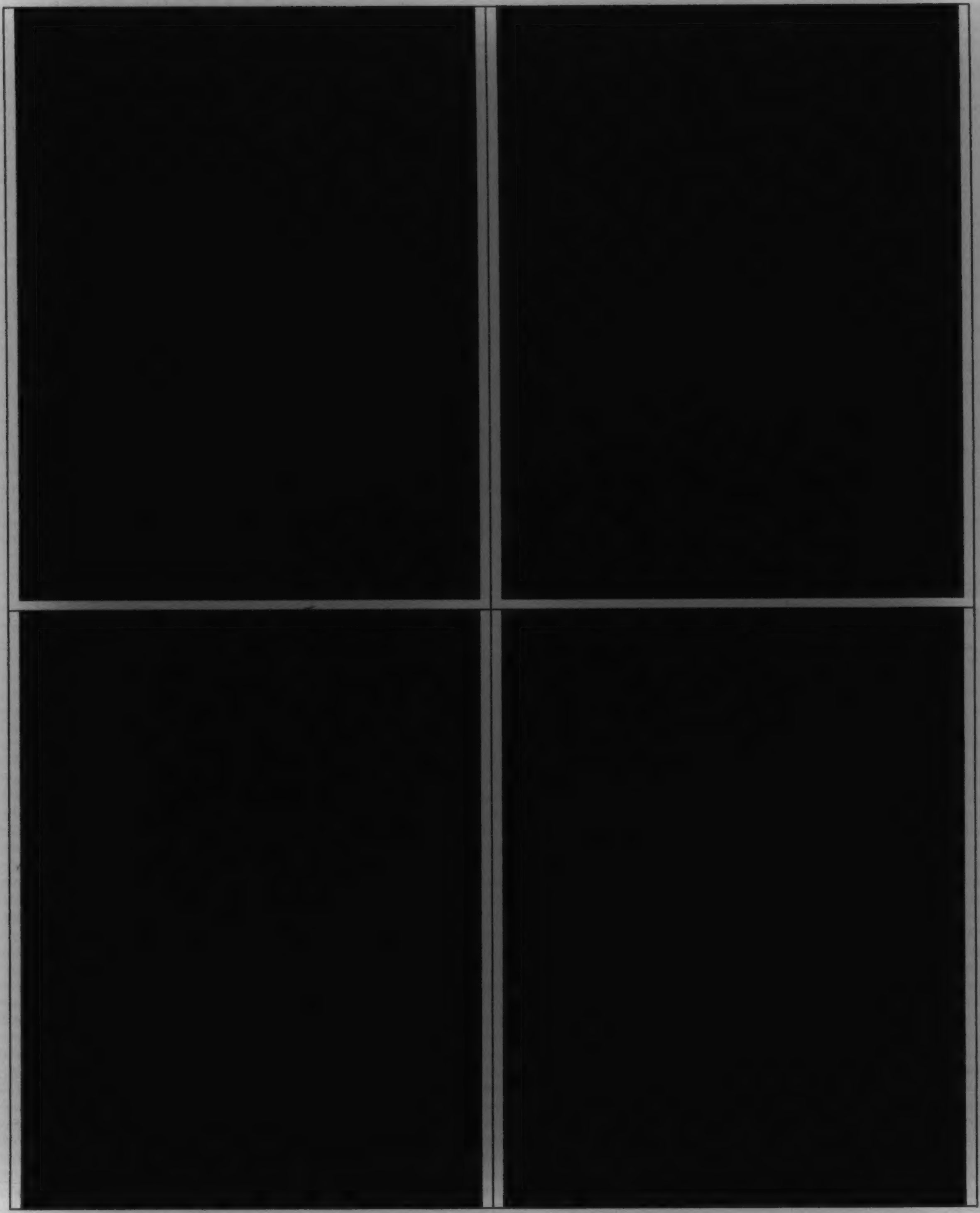


Fig 4.30: Microscopic analysis of froth from poor ore with 4 ml kerosene at 50°C

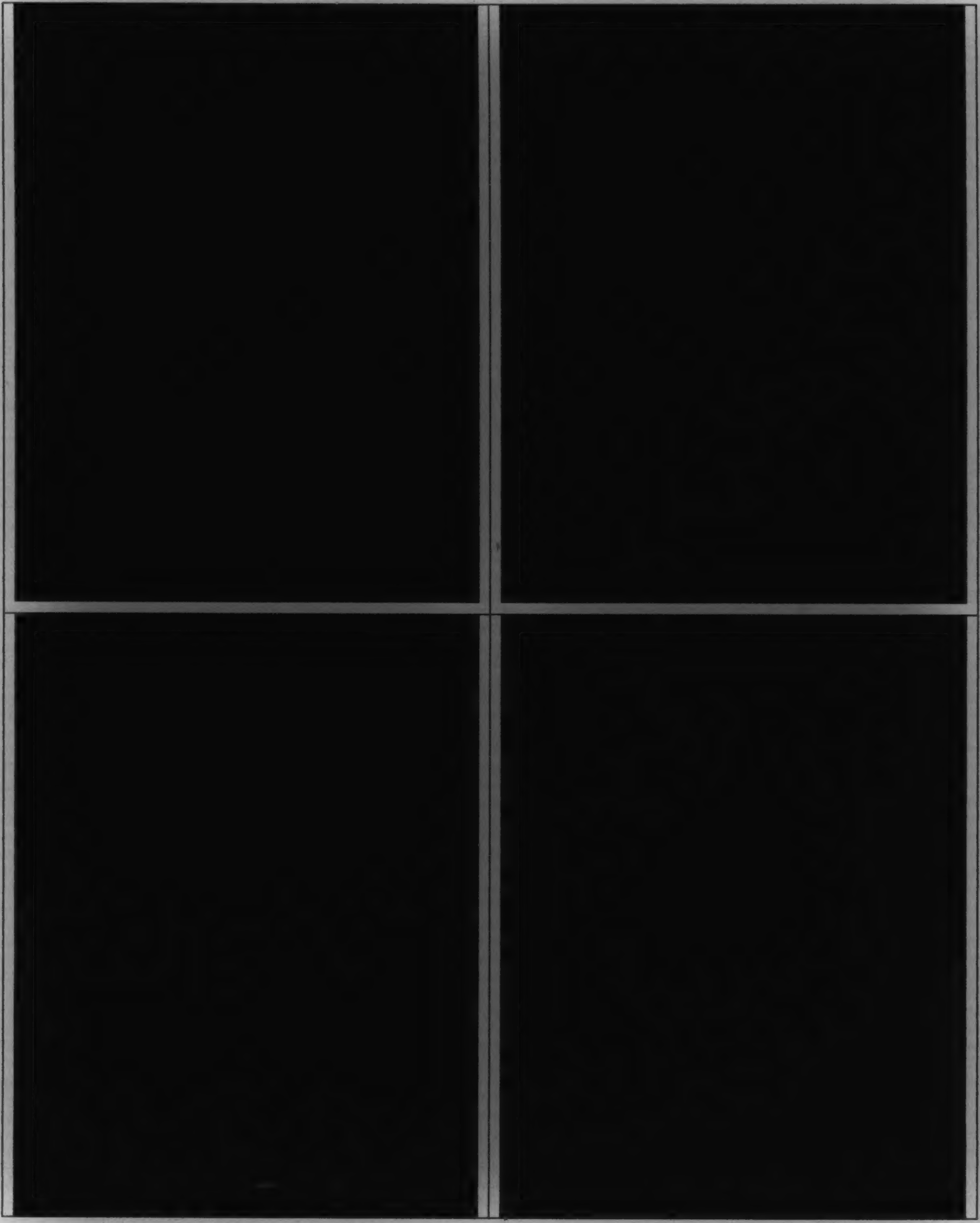


Fig 4.31: Microscopic analysis of froth from Poor ore with no solvent addition at 25°C

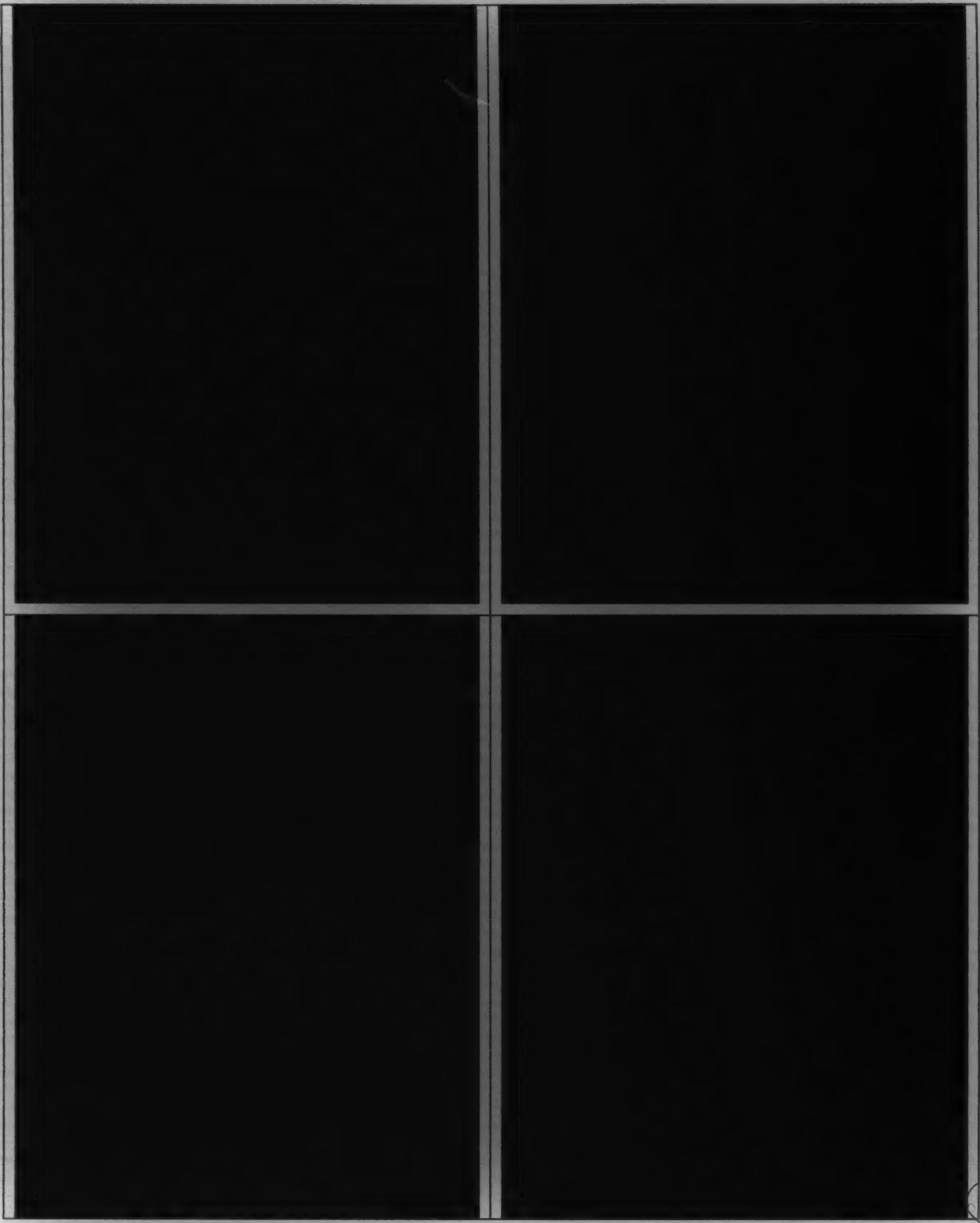


Fig 4.32: Microscopic analysis of froth from Poor ore with 4 ml kerosene at 25°C

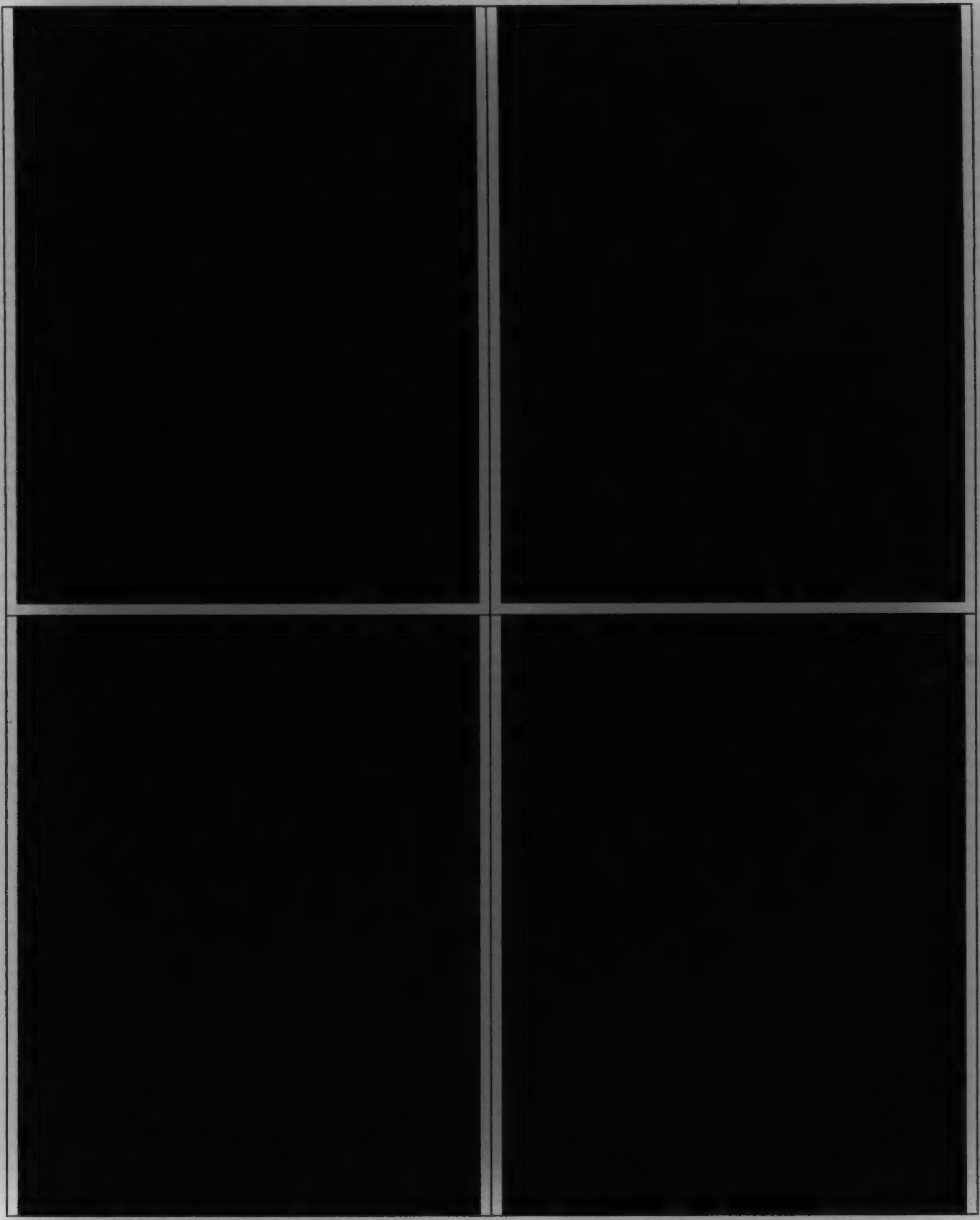


Fig 4.33: Microscopic analysis of froth from Poor ore with 15 ml kerosene at 25°C

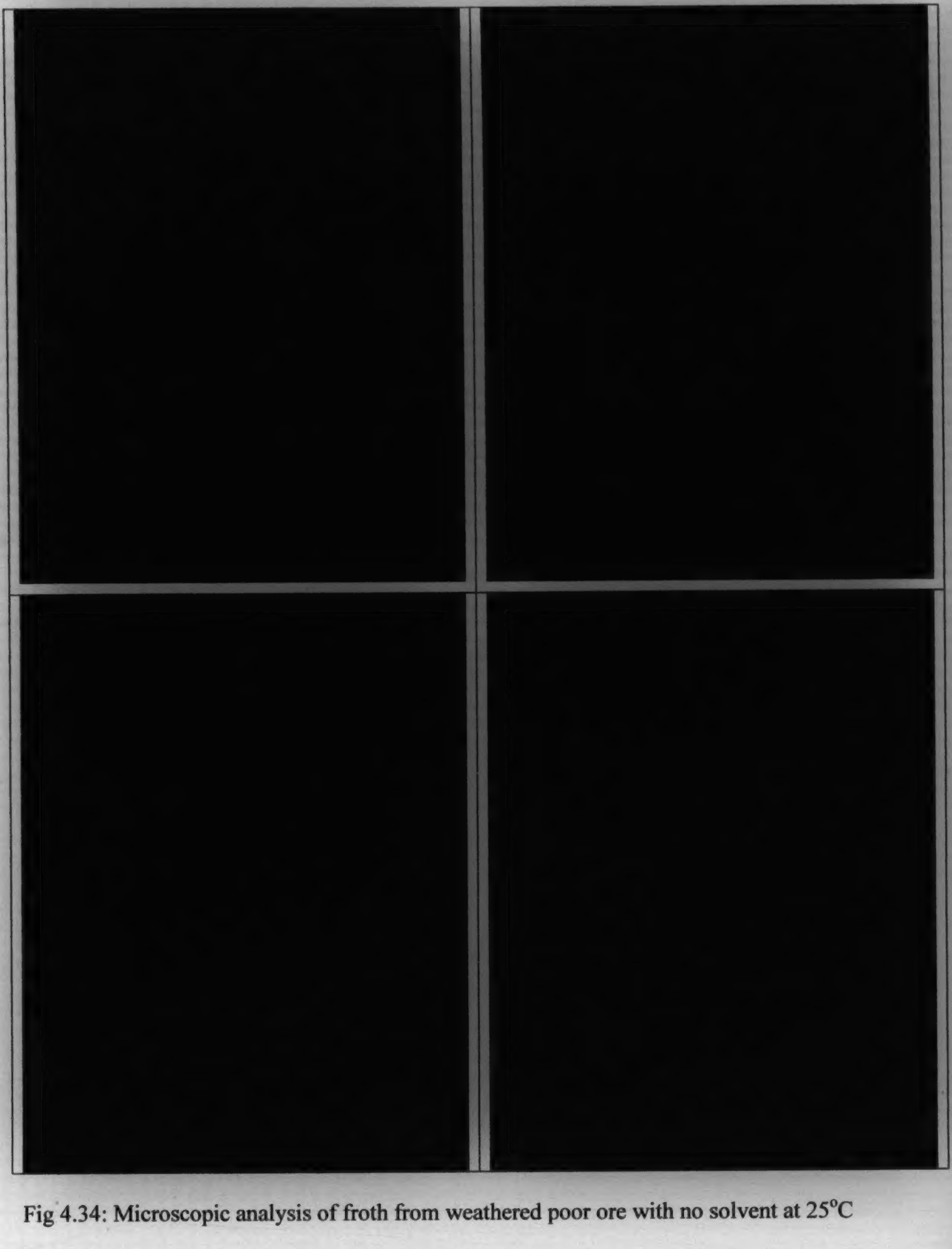


Fig 4.34: Microscopic analysis of froth from weathered poor ore with no solvent at 25^{o}C

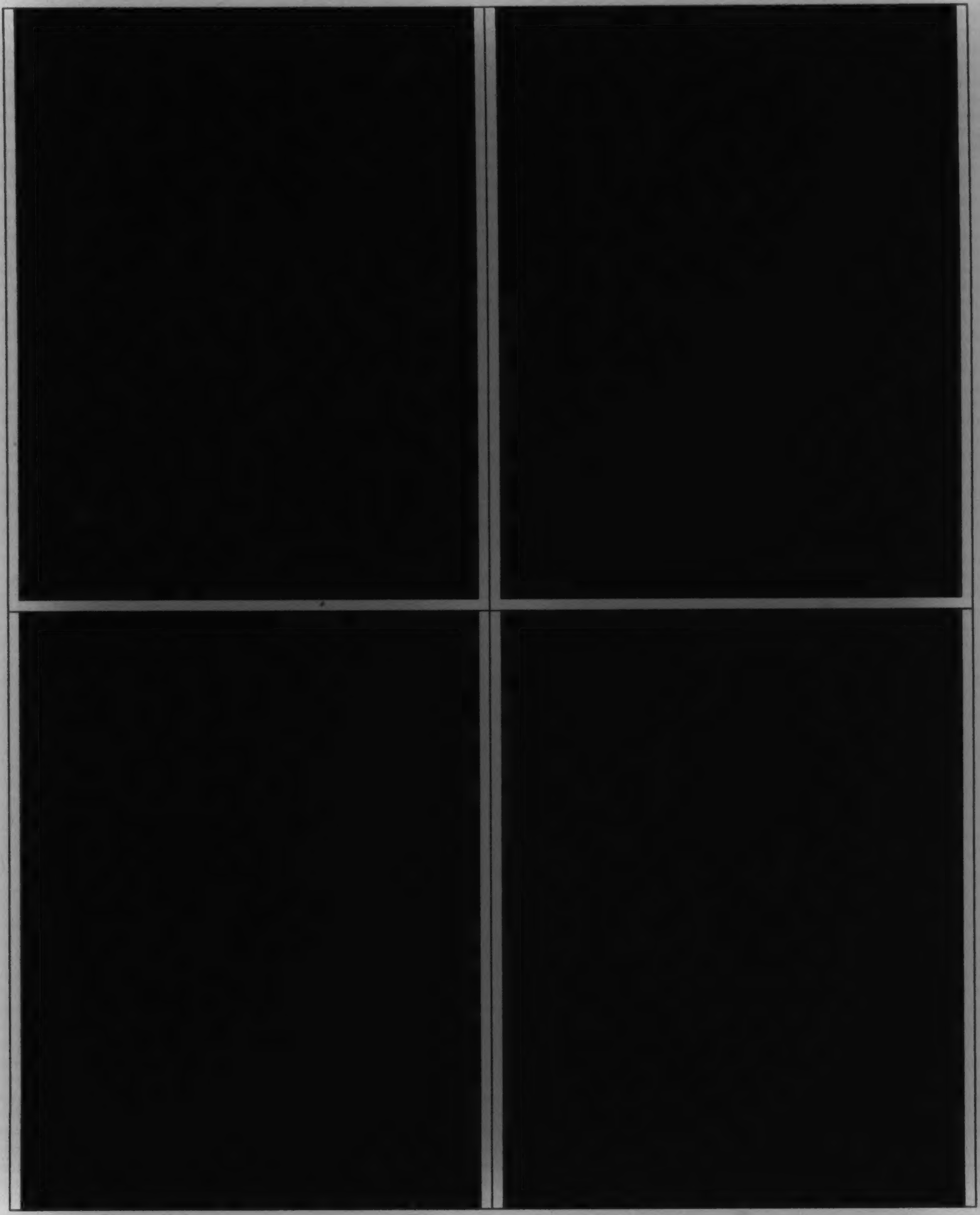


Fig 4.35: Microscopic analysis of weathered poor ore froth with 4 ml solvent at 25^{o}C

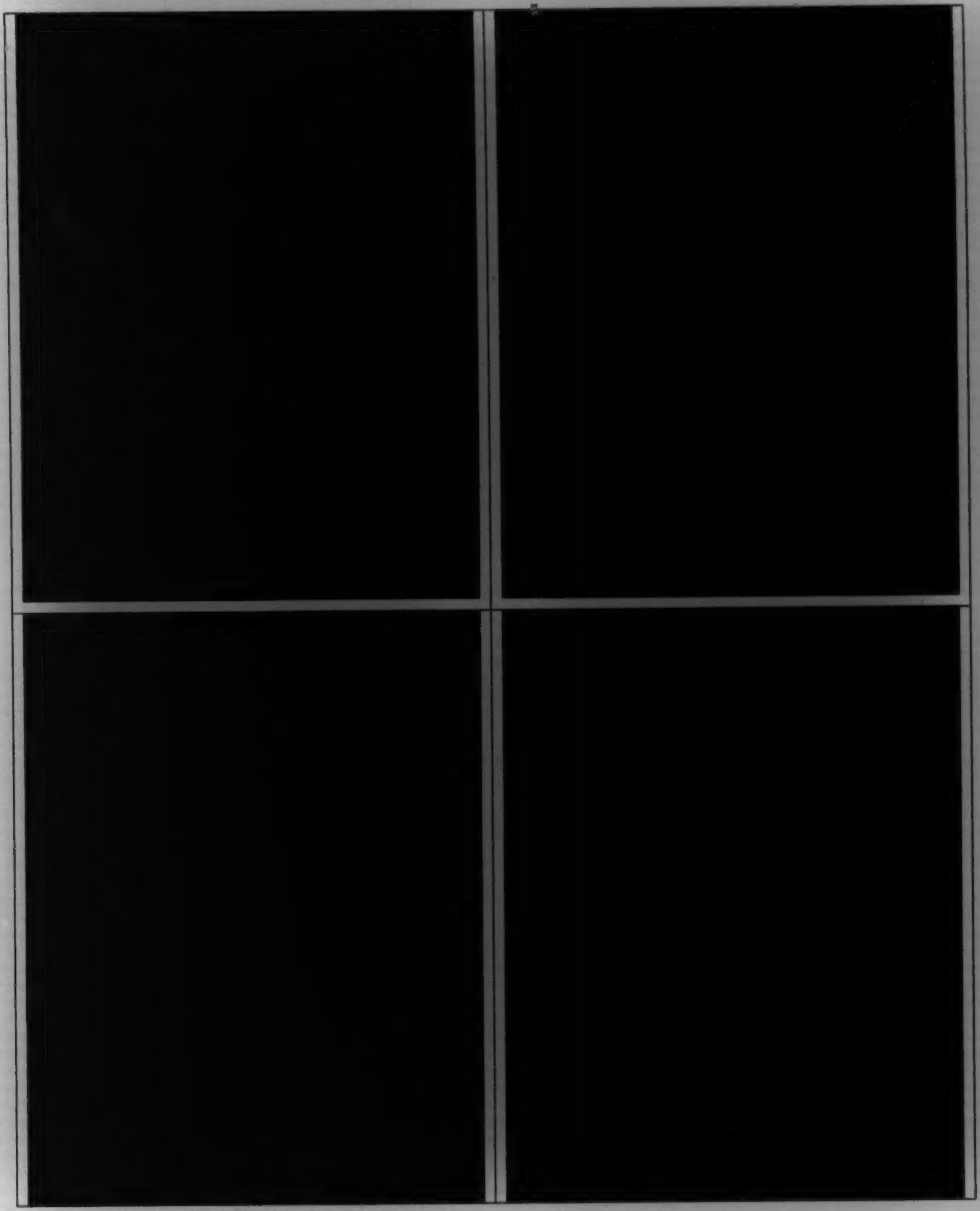


Fig 4.36: Microscopic analysis of weathered poor ore froth with 15 ml solvent at 25°C

4.8 SUMMARY: Naphtha as well as kerosene soaking in the ore proved beneficial both with respect to reduction in solids to bitumen ratio and improvement in the bitumen recovery. Depending on the type and characteristics of an ore, there is an optimal quantity of solvent that should be added in the ore to have maximum bitumen recovery and optimal reduction in solids in the froth. Figure 4.37 summarizes the impact of kerosene soaking in poor processing ore-A for 5 minutes and extraction done at 50°C and 25°C for 20 minutes recovery. Kerosene soaking in the ore improved the bitumen recovery upto around 2 ml additions and then decreased at higher levels of additions for 50°C extraction; however it improved with the kerosene addition at 25°C extraction. The solids to bitumen ratio decreased with the addition of kerosene in the ore at 50°C, however at 25°C, it increased initially upto around 2 ml of kerosene in ore and then decreased with higher addition.

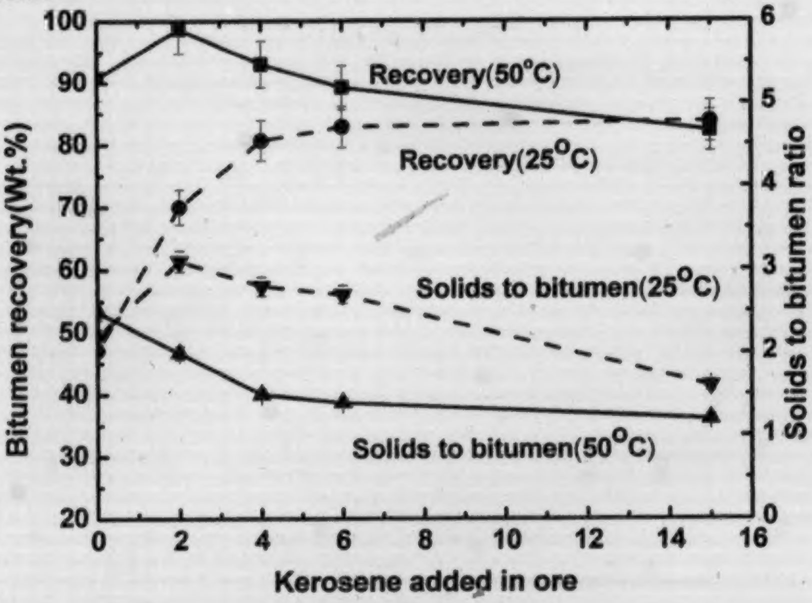


Figure 4.37: Comparison of bitumen recovery and solids to bitumen ratio for kerosene soaked in poor processing ore-A for 5 minutes and extraction done at 50°C and 25°C for 20 minutes recovery

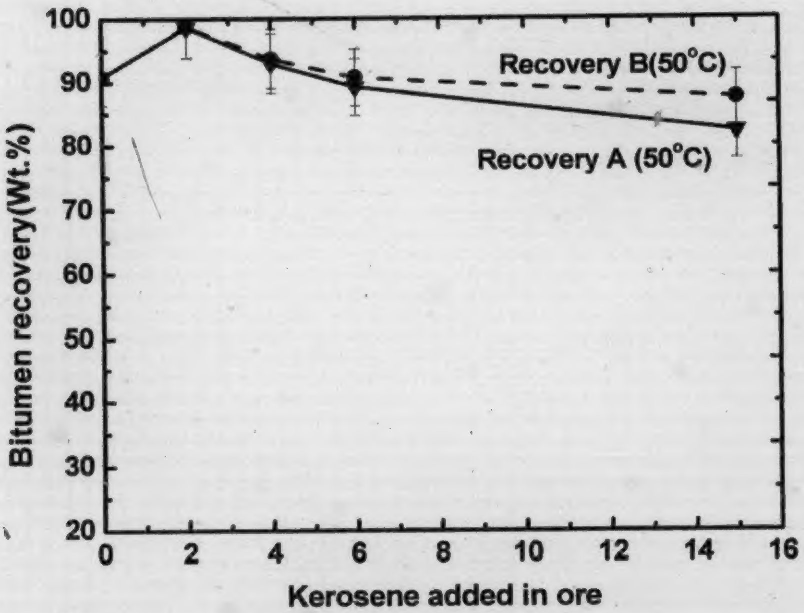


Figure 4.38: Bitumen recovery at 50°C from kerosene-soaked poor processing ore for 5 minutes. Case A: The amount of kerosene added in the ore is subtracted from the total recovered bitumen. Case B: Bitumen recovery based on total bitumen recovered with respect to bitumen present in the ore and kerosene added in the ore

A check was carried out for kerosene soaked in poor processing ore for 5 minutes and extraction carried out at 50°C to determine bitumen recovery based on total bitumen recovered with respect to bitumen present in the ore and kerosene added in the ore. This bitumen recovery still shows a decrease in bitumen recovery at 4-15 ml kerosene addition though the decrease is less as compared to the case for bitumen recovery where the quantity of kerosene added in the froth is subtracted from the total bitumen recovered as discussed in Figure 4.37. This finding suggests that higher addition levels of kerosene in the ore are leading to higher losses of kerosene and bitumen. These losses are probably due to emulsification of kerosene-soaked bitumen, leading to their loss to the tailings water or along with the solids in the tailings. The reason for the loss of both bitumen and kerosene at higher kerosene addition levels needs further research.

5. SUMMARY AND CONCLUSIONS

In this study, investigation has been carried out to analyze the impact of solvent addition to the oil sands or bitumen froth for improvement in bitumen recovery as well as solids reduction in the forth. Analysis has been conducted mainly at 50°C and 25°C with different type of oil sand ores and process water. Major conclusions and observations are given below:

A. IMPACT AT 50°C EXTRACTION

1) Kerosene or naphtha spray wash of the forth during froth generation from oil sand ores reduces the solids in the froth. The reduction in the solids is found to be:
    a) Highest in high fines ores.
    b) Appreciable in poor processing ores, which increases with the increase in solvent dosage.
    c) Negligible in case of weathered ores and no regular trend with the increase in solvent dosage.
    d) Minimal in case of good processing ores.
2) Kerosene or naphtha soaking in the ore before extraction indicates:
    a) Decrease in solids to bitumen ratio with the increasing solvent addition in the ore

b) The bitumen recovery increases at initial addition of the solvent and was observed to be highest at 2- 4 ml solvent addition on 300 g of ore and then started decreasing.

c) Total solids in the froth decreases with the solvent addition.

d) Coarse solids (>45μ) in the froth decrease more than the fines (<45μ).

e) Reduction in characteristic structures observed for poor processing ores bitumen froth images.

f) Kerosene loss to tailings water less than 1% of the quantity added in the ore.

g) No variation in the surface tension of tailings water.

h) No variation in the zeta potential of the fines in the solids recovered in the forth.

B. IMPACT AT 25°C EXTRACTION

3) Kerosene or naphtha soaking in the ore before extraction indicates:

a) Solids/bitumen ratio initially increased with the addition of solvent. It was maximum at 2-4ml of solvent (on 300 g of ore) and then decreased with further addition of solvent

b) Bitumen recovery improves with the solvent addition

c) Short soaking time is beneficial

d) Fine solids (>45μ) in the froth decreases more than the coarse solids (<45μ).

e) Reduction in characteristic structures observed for poor processing ores as well as weathered poor ores bitumen froth images.

f) Kerosene loss to tailings water less than 0.5% of the quantity added in the ore.

g) No variation in the surface tension of tailings water.

h) No variation in the zeta potential of the fines in the solids recovered in the forth

6. RECOMMENDATION AND FUTURE WORK

1. The experiments conducted at 25°C were based on addition of kerosene to the ore for soaking. Impact of addition of naphtha to oil sand ores on bitumen recovery and solids to bitumen ratio needs to be analyzed at 25°C extraction because naphtha spray washing of bitumen froth showed better results with respect to improvement in bitumen recovery and reduction in solids to bitumen ratio at 50°C.
2. The reason for the loss of bitumen recovery at higher levels of solvent addition at 50°C extraction.
3. Loss of kerosene in the tailings water has been conducted using gas chromatography by estimating carbon area count (C10-C20) in the tailings water sample. Alternative methods are to be checked to carry out extensive study to analyze the loss of kerosene in the tailings water as well as with the solids in the tailings water.
4. Morphology analysis has shown characteristic structures in the froth from poor processing ore and weathered poor processing ore as well. The images have also shown improvement in the bitumen froth morphology with the addition of kerosene in the ore. Extensive study needs to be done to analyze these characteristic structures and reasons for improvement in the morphology due to kerosene addition in the ore.

REFERENCES

Ali, L.H, "Studies on Aging Phenomenon of Tar Sand", Elsevier Sci Ltd, *Fuel* 54 (3): 223-223 (1975).

Anderson, W.G., "Wettability Literature Survey – Part 1:Rock/Oil/Brine Interactions and Effects of Core Handling on Wettability", *J. Petro. Technol.* 1125–1144 (1986).

Basu, S., K. Nandakumar and J. Masliyah, "A Study on Oil Displacement on Model Surfaces", *J. Colloid Interface Sci.* 1 8 2, 82–84 (1996).

Basu, S., K. Nandakumar and J. Masliyah, "On Bitumen Liberation from Oil Sands", *Can. J. Chem. Eng.* 75, 196–204 (1997).

Basu, S., K. Nandakumar and J. Masliyah, "A Visual Study of High Grade Oil Sand Disintegration Process", *J. Colloid Interface Sci.* 205, 201–203 (1998).

Bichard, J.A., "Oil Sands Composition and Behavior Research", The research papers of John A. Bichard 1957–1965, *AOSTRA technical publication* series 4, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1987).

Boon, J.A., "Fluid-Rock Interaction During steam Steam Injection", The Oil Sands of Canada-Venezuela, D.A.Redford and Winestock,A.G., Eds. Special Volume1, Ca. *Min. Metallurgy, Montreal*, pp.133-138 (1978).

Bowman, C.W., "Molecular and Interfacial Properties of Athabasca Tar Sands", Proc. 7th *World Petrol. Congr.* 3, 583–604 (1967).

Carrigy, M.A and Kramers, J.W., "Guide to the Athabasca Oil Sands Area', Alberta Research Council, (1973).

Clark, K.A., “The Separation of the Bitumen from Alberta Bituminous Sands”, *Can. Inst. Min. Metall.* Bull. 22, 1385–1395 (1929).

Clark, K.A. and D.S. Pasternack, “Hot Water Separation of Bitumen from Alberta Bituminous Sand”, *Ind. Eng. Chem.* 24, 1410–1416 (1932).

Clark, K. A., “Hot-Water Separation of Alberta Bituminous Sand”, Trans. *Can. Inst. Min. Metall.* 47, 257–274 (1944).

Clark, K. A.; Pasternack, D. S., “Hot water separation of bitumen from Alberta bituminous sand”, *Ind. Eng. Chem. Res.*, 24, 1410 (1985).

Dai, Q. and K. Chung, “Bitumen-Sand Interaction in Oil Sand Processing”, *Fuel* 74, 1858–1864 (1995).

Drelich, J., D. Lelinski, J. Hupka and J.D. Miller, “The Role of Gas Bubbles in Bitumen Release during Oil Sand Digestion”, *Fuel* 74, 1150–1155 (1995).

Drelich, J., D. Lelinski and J.D. Miller, “Bitumen Spreading and Formation of Thin Bitumen Films at a Water Surface”, *Colloids Surfaces* 116, 211–223 (1996).

Jan D. Miller, Dariusz Lelinski, Jaroslaw Drelich, and Jan Hupka, “ Rate of Bitumen Film Transfer from a Quartz Surface to an Air Bubble as Observed by Optical Microscopy”, *The Canadian Journal of Chemical Engineering*, Volume 82, (August 2004).

Hall, A.C., S.H. Collins, and J.C. Melrose, “Stability of Aqueous Wetting Films in Athabasca Tar Sands”, *Soc. Petrol. Eng. J.* 23: 249–258 (April 1983).

Hepler, L.G. and C. Hsi, “AOSTRA Technical Handbook on Oil Sands, Bitumen and Heavy Oils”, *AOSTRA technical publication* series 6, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1989).

Hepler, L.G. and R.G. Smith, "The Alberta Oil Sands: Industrial Procedures for Extraction and Some Recent Fundamental Research", *AOSTRA technical publication series 14*, Alberta Oil Sands Technology and Research Authority, Edmonton, AB (1994).

Hupka, J. and J. D. Miller, "Moderate-Temperature Water-Based Bitumen Recovery from Tar Sand," *Fuel* 70, 1308–1312 (1991).

Hupka, J., J. D. Miller and A. Cortes, "Importance of Bitumen Viscosity in the Hot Water Processing of Domestic Tar Sands," *Mining Eng.* 35, 1635–1641 (1983).

Hupka, J., A. G. Oblad and J. D. Miller, "Diluent-Assisted Hot-Water Processing of Tar Sands," *AOSTRA J.* 3, 95–102 (1987).

Hupka, J., J. D. Miller and Jaroslaw Drelich, "Water-based bitumen recovery from diluent-conditioned oil sands", *Canadian Journal Of Chemical Engineering*, 82 (5): 978-985 (2004).

Kasongo, T., Z. A. Zhou, Z. Xu and J. H. Masliyah, "Effect of Calcium Ions and Fine Clays on Bitumen Extraction from Athabasca Oil Sands Using Flotation", *Can. J. Chem. Eng.* 78, 674–681 (2000).

Kasperski, K.L., "A Review of Research on Aqueous Extraction of Bitumen from Mixed Oil Sands", *CETC-Devon*, 01-17 (2001).

Khraisha,Yahya H., "Study of Extraction and Pyrolysis of Jordan Tar Sand", *Int. J. Energy Res.*, 23, 833-839 (1999).

Liu, J., T. Mak, Z. A. Zhou and Z. Xu, "Fundamental Study of Reactive Oily-Bubble Flotation", *Minerals Engin.* 15, 667–676 (2002).

Liu, J., Z. Xu and J. Masliyah, "Role of Fine Clays in Bitumen Extraction from Oil Sands", *AIChE* 50, 1917–1927 (2004).

Luthra, M., Robert J.G. Lopetinsky, R. Sean Sanders, K. Nandkumar and Jacob Masliyah, "A New Device to Determine Bitumen Extraction from Oil Sands", *Can. J. Chem. Eng.*, 82, 752-762 (2004).

Masliyah, J.H., "Intensive Short Course on Extraction of oil Sands Bitumen", Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB (June 2000).

Masliyah. J, Zhiang (Joe) Zhou, Zhenghe Xu, Jan Czarnecki and Hassan Hamza, "Understanding Water-Based Bitumen Extraction from Athabasca Oil Sands", *The Canadian Journal of Chemical Engineering,* Volume 82, (2004).

Miller, J.D. and M. Misra, "Hot Water Process Development for Utah Tar Sands", *Fuel Process. Technol.* 6, 27–59 (1982).

Moran, K., A. Yeung, "Determining Bitumen Viscosity through Drop Shape Recovery", *Canadian Journal Of Chemical Engineering*, 82 (4): 813-820 (2004).

Munoz, V.A., K.L. Kasperski, O.E. Omostoso and R.J. Mikula, " The use of Microscopic Bitumen Froth Morphology for the identification of problem Oil Sand Ores', *Petroleum Science and Technology*, 21, (99-10), 1509-1529 (2003).

Sanford, E.C. and F.A. Seyer, "Processability of Athabasca Tar Sand Using a Batch Extraction Unit: The Role of NaOH", *CIM Bul*, 3.164–169 (March 1979).

Sanford, E.C., "Processabilty of Athabasca Oil Sand: Interrelationship between Oil Sand Fine Solids, Process Aids, Mechanical Energy and Oil Sand Age After Mining", *Can. J. Chem. Eng.* 6 1, 554–567 (1983).

Schramm, L.L., C. Morrison and E.N. Stasiuk, "Some Effects of Chemical Additions to Nascent Primary Froth from the Hot Water Flotation of Bitumen from Athabasca Oil Sand", *Fuel Process. Technol.* 56, 243–261 (1998).

Schramm, L.L., E.N. Stasiuk, "The Influence of solvent and demulsifier additions on nascent froth formation during flotation recovery of Bitumen from Athabasca oil sands", *Fuel Processing Technology.* 73, 95–110 (2001).

Sepulveda, J.E. and J.D. Miller, "Separation of Bitumen from Utah Tar Sands by a Hot Water Digestion-Flotation Technique", *Mining Engineering.* 30, 1311–1320 (1978).

Seyer, F.A. and C.W. Gyte, "Viscosity" in "AOSTRA Technical Handbook on Oil Sands, Bitumens and Heavy Oils", *AOSTRA Technical Publication* Series # 6 (1989).

Shuyuan, L., Jianqiu, W., Huaping, T. and Zhaoliang, W., "Study of extraction and pyrolysis of Chinese oil sands", *Fuel,* 74, 1191-1193 (1995).

Su, Li., Zhenghe Xu , Jacob Masliyah, "Role of oily Bubbles in Enhancing Bitumen Recovery", *Minerals Engineering,* 19, 641–650 (2006).

Sury, K.N., "Low Temperature Bitumen Recovery Process", US patent 4 946 597 (August 1990).

Takamura, K., "Microscopic Structure of Athabasca Oil Sand", *Can. J. Chem. Eng.* 60, 538–545 (1982).

Waldemar I. Friesen, Tadeusz Dabros, and Teddy Kwong, "A Bench Scale Study of Conditioning Behaviour in Oil Sands Slurries", *Can. J. Chem. Eng.*, 82 743–751 (2004).

Wallwork, V., Z. Xu and J. Masliyah, "Bitumen Recovery with Oily Air Bubbles", *Can. J. Chem. Eng.* 81, 993–997 (2003).

Wallwork, V., Z. Xu and J. Masliyah, " Processibilty of Athabasca Oil Sand Using a Laboratory Hydrotransport Extraction System (LHES)", *Can. J. Chem. Eng.*, 82 687–695 (2004).

Zhou, Z.A., T. Kasongo, Z. Xu and J.H. Masliyah, "Assessment of Bitumen Recovery from the Athabasca Oil Sands Using a Laboratory Denver Flotation Cell", submitted to *Can. J. Chem. Eng.*, 82, 696–703 (2004).

Zhou, Z. A., H. Li, Z. Xu, and J. H. Masliyah, "Role of Acidified Sodium Silicate in Low Temperature Bitumen Extraction from Poor-Processing Oil Sand Ores", *Ind. Eng. Chem. Res.* 44, 4753-4761 (2005).

APPENDIX A

This appendix contains the tabulated and inferred data for all the experimental work carried out for this study. The tabulated data represents the data used for various figures shown in the thesis.

Table A.1: Tabulated data for Figure 3.2: Bitumen froth analysis data for different solvent washing of froth scooped from the top of jar for jar test

Froth composition	**Suncor poor processing Ore**			**Syncrude poor processing ore**		
	No Solvent	**2 ml Kerosene**	**2 ml Naphtha**	**No Solvent**	**2ml Kerosene**	**2 ml Naphtha**
Solids (g)	1.7	1.4	0.9	0.6	0.3	0.2
Water (g)	25.5	22.8	24.1	18.3	17.6	17.5
Bitumen in 5ml (g)	0.1	0.1	0.1	0.0	0.0	0.0
Bitumen in 250 ml (g)	2.9	2.7	3.1	0.6	0.5	0.6
Total (g)	30.2	26.9	28.1	19.5	18.3	18.3
Solids to Bitumen Ratio	**0.59**	**0.54**	**0.28**	**1.05**	**0.54**	**0.34**

Table A.2: Tabulated data for Figure 3.3: Bitumen froth analysis data for different solvent washing of froth for High Fines ore at 50°C

Solvent	Solvent		Froth composition (g)			Solids /Bitumen
	(ml)	(g)#	Water	Solids	Bitumen	
Naphtha	0	0.0	51.4	65.1	37.8	1.7
	3	2.0	44.6	32.1	39.5	0.8
	6	3.9	46.9	32.0	38.4	0.8
	9	5.9	53.2	29.8	39.0	0.8
Kerosene	0	0.0	51.4	65.1	37.8	1.7
	3	2.4	41.4	42.3	38.2	1.1
	6	4.8	50.4	35.3	41.0	0.9
	9	7.2	62.4	32.8	43.8	0.7
Naphtha in 30 ml PW	0	0.0	42.1	57.6	38.0	1.5
	3	2.0	39.9	49.6	36.3	1.4
	6	3.9	37.0	42.0	37.4	1.1
	9	5.9	42.4	35.1	38.4	0.9
Kerosene in 30 ml PW	0	0.0	42.1	57.6	38.0	1.5
	3	2.4	34.8	45.8	36.9	1.2
	6	4.8	42.1	42.1	43.0	1.0
	9	7.2	48.1	31.0	41.0	0.8

# Naphtha density: 640 kg/m^3 and Kerosene density: 800 kg/m^3

Table A.3: Tabulated data for Figure 3.5: Bitumen froth analysis data for naphtha washing of froth using syringe and spray for poor processing ore at 50^{o}C

Solvent	Naphtha		Froth composition (g)			Solids /Bitumen
	(ml)	(g)	Water	Solids	Bitumen	
Naphtha (Syringe wash)	0	0	145.9	50.5	14.7	3.4
	2	1.3	143.3	43.6	14.8	2.9
	4	2.6	142.9	38.6	15.1	2.6
	6	3.9	143.8	39.0	16.0	2.4
Naphtha (Spray wash)	0	0	145.9	50.5	14.7	3.4
	2	1.3	138.2	43.8	15.2	2.9
	4	2.6	141.9	39.6	15.6	2.5
	6	3.9	144.6	37.8	15.8	2.4

Table A.4: Tabulated data for Figure 3.6: Bitumen froth analysis data for naphtha spray washing of froth for poor processing ore and naturally weathered poor processing ore at 50°C

Ore	**Naphtha**		**Froth composition (g)**			**Solids /Bitumen**
	(ml)	**(g)**	**Water**	**Solids**	**Bitumen**	
Poor Processing Ore	0	0	145.9	50.5	14.7	3.4
	2	1.3	138.2	43.8	15.2	2.9
	4	2.6	141.9	39.6	15.6	2.5
	6	3.9	144.6	37.8	15.8	2.4
Naturally weathered Poor Processing Ore	0	0	69.4	95.1	32.4	2.9
	2	1.3	65.9	91.5	31.8	2.9
	4	2.6	73.3	97.8	31.9	3.1
	6	3.9	63.9	86.0	31.2	2.8

Table A.5: Tabulated data for Figure 3.7: Bitumen froth analysis data for naphtha spray washing of froth for good processing ore and artificially weathered good processing ore at 50^oC

Ore	**Naphtha**		**Froth composition (g)**			**Solids /Bitumen**
	(ml)	**(g)**	**Water**	**Solids**	**Bitumen**	
Good Processing Ore	0	0	20.5	4.5	42.9	0.10
	2	1.3	20.4	4.4	40.2	0.11
	4	2.6	24.2	4.4	43.6	0.10
	6	3.9	27.3	4.3	41.2	0.10
Artificially weathered good processing Ore	0	0	22.5	20.5	42.7	0.48
	2	1.3	27.2	18.7	42.1	0.44
	4	2.6	24.6	21.7	42.2	0.51
	6	3.9	28.8	23.6	42.6	0.55

Table A.6: Tabulated data for Figure 3.8: Solids recovered in froth for naphtha spray washing of froth at 50°C and 35°C for poor processing ore

Ore and Operating temperature	**Naphtha Qty. (ml)**	**Solids recovered in froth (g)**	**% Reduction in solids (Wt.%)**
Poor processing ore at 50°C	0	50.9	0
	2	42.5	16.5
	4	39.3	22.9
	6	37.5	26.4
Poor processing ore at 35°C	0	70.8	0
	2	56.5	20.1
	4	54.2	23.4
	6	53.5	24.3

Table A.7: Tabulated data for Figure 3.9: Particle size distribution of solids in the naphtha washed froth at 35°C extraction for poor processing ore

Naphtha (ml)	**0**	**2**	**4**	**6**
Coarse solids in g (Solids > 45 μm)	25.7	24.9	22.4	22.4
Fines in g (Solids < 45 μm)	45.1	31.6	31.9	31.2
Total solids in g	70.8	56.5	54.2	53.5

Table A.8: Tabulated data for Figure 3.10: Particle size distribution of solids in the naphtha washed froth at 50°C extraction for poor processing ore

Naphtha (ml)	**0**	**2**	**4**	**6**
Coarse solids in g (Solids > 45 μm)	18.1	14.8	12.1	11.6
Fines in g (Solids < 45 μm)	32.8	27.8	27.2	25.9
Total Solids in g	50.9	42.5	39.3	37.5

Table A.9: Tabulated data for Figure 3.12: Bitumen froth analysis data for naphtha and heptol spray washing of froth at 50°C for poor processing ore

Solvent	**Solvent**	**Froth Composition (g)**			**Solids /Bitumen**
	(ml)	**Water**	**Solids**	**Bitumen**	
Naphtha	0	145.9	50.5	14.7	3.4
	2	138.2	43.8	15.2	2.9
	4	141.9	39.6	15.6	2.5
	6	144.6	37.8	15.8	2.4
Heptol	0	145.9	50.5	14.7	3.4
	2	151.2	40.5	14.8	2.7
	4	147.6	38.0	15.0	2.5
	6	169.2	34.3	15.1	2.3

Table A.10: Tabulated data for Figure 3.13: Bitumen froth analysis data for naphtha washing of froth at $50^{o}C$ for different ores

Ore	Naphtha		Froth Composition (g)			% Wt. Reduction in solids
	(ml)	(g)	Water	Solids	Bitumen	
High fines ore	0	0	51.4	65.1	37.8	0.0
	2	1.3	44.6	32.1	39.5	50.7
	4	2.6	46.9	32	38.4	50.8
	6	3.9	53.2	29.8	39	54.2
Poor processing ore	0	0	145.9	50.5	14.7	0.0
	2	1.3	138.2	43.8	15.2	13.3
	4	2.6	141.9	39.6	15.6	21.6
	6	3.9	144.6	37.8	15.8	25.1
Naturally weathered poor ore	0	0	69.4	95.1	32.4	0.0
	2	1.3	65.9	91.5	31.8	3.8
	4	2.6	73.3	97.8	31.9	-2.8
	6	3.9	63.9	86	31.2	9.6
Good processing ore	0	0	20.5	4.5	42.9	0.0
	2	1.3	20.4	4.4	40.2	2.2
	4	2.6	24.2	4.4	43.6	2.2
	6	3.9	27.3	4.3	41.2	4.4
Artificially weathered good ore	0	0	22.5	20.5	42.7	0.0
	2	1.3	27.2	18.7	42.1	8.8
	4	2.6	24.6	21.7	42.2	-5.9
	6	3.9	28.8	23.6	42.6	-15.1

Table A.11: Inferred data for Figure 3.13: Percentage reduction in solids in the recovered froth for naphtha spray for different ores froth at 50°C using data given in table A.9

Solvent	**% Wt. reduction in solids in the recovered froth**				
Naphtha (ml)	**High fines ore**	**Poor processing ore**	**Naturally weathered poor ore**	**Good processing ore**	**Artificially weathered good ore**
0	0.0	0.0	0.0	0.0	0.0
2	50.7	13.3	3.8	2.2	8.8
4	50.8	21.6	-2.8	2.2	-5.9
6	54.2	25.1	9.6	4.4	-15.1

Table A.12: Tabulated data for Figure 4.1 and 4.2

Poor Processing Ore	Bitumen recovery		Solids to bitumen ratio	
	Naphtha spray	Naphtha soak	Naphtha spray	Naphtha spray
A	61.4	75.5	2.0	1.0
B	72.7	75.7	1.2	0.9

Table A.13: Tabulated data for Figure 4.3

Kerosene added (ml)	Bitumen recovery	Solids to bitumen ratio
0	91.2	0.12
2	98.9	0.09
4	95.3	0.09
6	92.2	0.09

Table A.14: Tabulated data for Figure 4.4 and 4.5

Solvent added (ml)	Bitumen recovery		Solids to bitumen ratio	
	Naphtha	Kerosene	Naphtha	Kerosene
0	80.4	80.4	3	3
2	83.9	92.6	2.6	2.4
4	84.7	88.1	2.2	2.3
6	80.1	85.3	2.2	2.2
15	75.5	69.3	1	0.9

Table A.15: Tabulated data for Figure 4.6 and 4.7

Solvent added (ml)	**Bitumen recovery**		**Solids to bitumen ratio**	
	Naphtha	**Kerosene**	**Naphtha**	**Kerosene**
0	85.8	85.8	2.6	2.6
2	89.2	89.9	2.3	1.9
4	93.3	83.8	2.3	2.0
6	84.0	78.2	1.8	1.6
15	75.7	77.7	0.9	1.0

Table A.16: Tabulated data for Figure 4.8

Flotation time (minutes)	**Bitumen recovery wt.%**			
	Kerosene added in ore (ml)			
	0.0	**2.0**	**4.0**	**6.0**
0.0	0.0	0.0	0.0	0.0
2.0	7.8	60.3	78.5	77.3
5.0	19.4	83.1	94.1	94.9
10.0	44.0	95.6	98.2	95.4
20.0	80.4	99.5	98.2	95.4

Table A.17: Tabulated data for Figure 4.9 & 4.10

Kerosene added (ml)	**Bitumen recovery**		**Solids to bitumen ratio**	
	10 minutes	**20 minutes**	**10 minutes**	**20 minutes**
0	44.0	80.4	0.2	0.1
2	95.6	99.5	0.1	0.1
4	98.2	98.2	0.1	0.1
6	95.4	95.4	0.1	0.1

Table A.18: Tabulated data for Figure 4.11

Flotation time (minutes)	**Bitumen recovery wt.%**				
	Kerosene added in ore (ml)				
	0.0	**2.0**	**4.0**	**6.0**	**15**
0.0	0.0	0.0	0.0	0.0	0.0
2.0	13.2	27.2	36.5	36.4	36.0
5.0	21.2	45.2	60.6	63.0	64.2
10.0	30.5	58.1	72.4	75.6	75.7
20.0	47.0	70.0	80.6	82.8	83.7

Table A.19: Tabulated data for Figure 4.12 & 4.13

Kerosene added (ml)	**Bitumen recovery**		**Solids to bitumen ratio**	
	10 minutes	**20 minutes**	**10 minutes**	**20 minutes**
0	30.5	47.0	2.3	2.2
1	45.8	58.5	3.2	2.6
2	58.1	70.0	3.4	3.1
3	67.8	73.9	3.1	2.9
4	72.4	80.6	2.9	2.8
6	75.6	82.8	2.7	2.7
15	75.7	83.7	1.6	1.6

Table A.20: Tabulated data for Figure 4.14

Flotation time (minutes)	**Bitumen recovery wt.%**				
	Kerosene added in ore (ml)				
	0.0	**2.0**	**4.0**	**6.0**	**15**
0.0	0.0	0.0	0.0	0.0	0.0
2.0	12.0	15.0	24.3	25.2	30.2
5.0	19.2	31.6	45.6	51.5	57.0
10.0	30.5	52.8	69.0	65.4	71.7
20.0	47.0	65.8	78.9	75.9	78.0

Table A.21: Tabulated data for Figure 4.15 & 4.16

Kerosene added (ml)	**Bitumen recovery**		**Solids to bitumen ratio**	
	10 minutes	**20 minutes**	**10 minutes**	**20 minutes**
0	30.5	47.0	2.3	2.2
1	43.7	58.9	3.0	2.8
2	52.8	65.8	3.5	3.3
4	69.0	78.9	3.0	2.9
6	65.4	75.9	2.3	2.3
15	71.7	78.0	1.7	1.7

Table A.22: Tabulated data for Figure 4.17

Flotation time (minutes)	**Bitumen recovery wt.%**				
	Kerosene added in ore (ml)				
	0.0	**2.0**	**4.0**	**6.0**	**15**
0.0	0.0	0.0	0.0	0.0	0.0
2.0	12.0	26.6	24.3	16.4	30.2
5.0	19.2	69.7	63.4	51.5	57.0
10.0	30.4	79.3	73.6	67.6	70.4
20.0	47.2	88.1	82.7	75.8	75.6

Table A.23: Tabulated data for Figure 4.18 & 4.19

Kerosene added (ml)	**Bitumen recovery**		**Solids to bitumen ratio**	
	10 minutes	**20 minutes**	**10 minutes**	**20 minutes**
0	30.4	47.2	2.3	2.1
2	69.2	69.2	2.3	2.5
4	71.9	79.0	2.8	2.7
6	68.7	76.2	2.9	2.8
15	65.2	69.3	2.9	2.9

Table A.24: Tabulated data for Figure 4.20

Flotation time (minutes)	**Bitumen recovery wt.%**				
	Kerosene added in ore (ml)				
	0.0	**2.0**	**4.0**	**6.0**	**15**
0.0	0.0	0.0	0.0	0.0	0.0
2.0	1.2	0.2	4.6	4.8	22.0
5.0	2.2	4.0	11.5	15.6	40.2
10.0	4.2	8.8	20.1	28.2	53.0
20.0	6.8	17.2	32.0	40.4	60.2

Table A.25: Tabulated data for Figure 4.21 & 4.22

Kerosene added (ml)	**Bitumen recovery**		**Solids to bitumen ratio**	
	10 minutes	**20 minutes**	**10 minutes**	**20 minutes**
0	4.2	6.8	8.3	8.2
2	8.8	17.2	6.5	5.4
4	20.1	32.0	5.9	5.1
6	28.2	40.4	5.5	4.8
15	53.0	60.2	4.4	4.4

Table A.26: Tabulated data for Figure 4.23

Kerosene added (ml)	**Fines in solids in the recovered bitumen froth (% wt.)**	
	50°C	**25°C**
0	18.7	25.8
2	17.6	17.0
4	23.5	16.1
6	24.2	16.0
15	26.9	15.4

Table A.27: Tabulated data for Figure 4.24

Kerosene added (ml)	**Fines in solids in the recovered bitumen froth (% wt.)**		
	Good ore	**Poor ore**	**Weathered poor ore**
0	32.4	25.8	36.3
2	13.8	17.0	20.6
4	15.4	16.1	14.9
6	15.2	16.0	14.8
15	14.5	15.4	14.5

Table A.28: Tabulated data for Figure 4.37

Kerosene added (ml)	**Bitumen recovery**		**Solids to bitumen ratio**	
	50°C	**25°C**	**50°C**	**25°C**
0	90.8	47	2.5	2.2
2	98.7	70	2	3.1
4	93	80.6	1.5	2.8
6	89.2	82.8	1.4	2.7
15	82.2	83.7	1.2	1.6

APPENDIX B

This appendix contains standard procedures used for operating Denver cell for bitumen froth generation from oil sand ores and Dean Stark method for analyzing the froth composition. (Source: Fundamentals of Oil Sands Extraction course)

B.1: STANDARD PROCEDURE FOR BITUMEN FLOTATION TESTS USING A DENVER FLOTATION CELL

1. Check the flotation cell. Make sure that the air supply to the flotation cell is connected, the air inlet valve is close and the agitation rate is set at the desired speed say, 1500 rpm.
2. Connect the water jacket of 1-Litre flotation cell with the thermal heating system, and adjust the temperature at a desired value say, 50°C.
3. Heat 1-L process water on a hot plate to a desired value say, 50°C and maintain constant mixing using a magnetic stirrer during the heating.
4. De-frost a bag of oil sands sample after removing it from freezer for 3-4 hour. Mix the sample well and weigh 300 gm of oil sands from the bag for the bitumen flotation test.
5. Put 950 ml of the process water at a given temperature into the flotation cell and add 300 gm of the oil sands into the water uniformly. Use a spatula to remove any oil sands staying on the stator of the flotation shaft immersed in the water.
6. Start agitation and maintain it for 5 minutes without airflow during oil sand conditioning stage.
7. Open the airflow valve at desired airflow rate (150 ml/min. air) and start timing the flotation period.
8. Use a spatula to collect bitumen froth floating on the slurry surface into a glass container or directly into the thimbles for next 10 or 20 minutes.

9. Separate thimbles can be used for containing first 2 minutes followed by next 3 minutes, 5 minutes and 10 minutes froth generated during the aeration process for further analysis of the froth using Dean Stark analysis.
10. Turn off the aeration and then the agitation.
11. Switch off the thermal heating system of the flotation cell, raise the flotation shaft/agitator and transfer the flotation tailings to a separate container.
12. Rinse the flotation cell with tap water to remove the sands, and put the cell back to the stand.
13. Put sufficient amount of toluene into the cell, turn on the agitator and let it run for few minutes to remove and wash away any bitumen sticking on the shaft, inside the rotator and on the cell. Clean the shaft and cell using paper towels.
14. Weigh the bitumen froth product and use it for further analysis.

B.2: STANDARD PROCEDURE FOR DEAN STARK METHOD FOR ANALYZING THE FROTH COMPOSITION

1. Add approximately 200 ml of toluene to each of the three or more distillation flasks used in Dean Stark apparatus.

[illegible] Label and place a thimble into a labeled glass jar for each of the three or more froth samples to be analyzed. Add 2 Kim wipes in each of the thimbles. Kim wipes are used to wipe any bitumen left in the bread pan.

3. Weigh Kim wipes, thimble and jar for each sample.
4. Carefully transfer the collected froth from the bread pans into the thimbles or directly from the flotation cell to each thimble using a spoon.

5. Using the Kim wipes, wipe the remaining sample from the pan and add the Kim wipes into the thimble.
6. Weigh individually the three jars containing the froth sample (in the thimbles).
7. Transfer the thimbles to the distillation flasks using the baskets and hang on the adapter. Make sure to cover the top of the thimble with the small screen before inserting them into the distillation flask.
8. Attach the trap and condenser to each distillation flask. Ensure that the trap stopcock is closed.
9. Turn on the condenser cooling water and ensure a good rate of water through the condensers.
10. Turn on the heating mantles to level 9 to heat the distillation flasks to boiling and refluxing.
11. Label and weigh each of the three or four plastic water bottles. Each bottle is for respective Dean Stark distillation flasks for collecting water from the water trap.
12. As water is collected in the trap, the level may raise to the top of the trap. Drain some of the water into the water bottle to again see an interface between the toluene and the water.
13. Continue refluxing for the time until the toluene dripping from the thimble is colorless. Periodically check the bottom of the flask so it does not get too low. Add toluene if necessary.
14. Turn off the mantles and leave condenser water on until the apparatus is cool. Let the apparatus cool for 6-8 hours.
15. Collect the water from the traps and weigh the plastic bottles.

16. Empty the traps into the toluene waste container.

17. Transfer the thimbles back into the glass jars and place in the vacuum oven to dry over night.

18. Transfer the liquid from the Dean Stark to 250 ml volumetric flasks, rinse with toluene wash bottle and ensure not to over fill the flask past the volumetric mark.

19. Allow the flask to cool and add toluene to the 250 ml mark.

20. Shake the flasks holding the stopper.

21. Weigh the dry filter paper.

22. Pipette 5 ml from the 250 ml flask onto filter paper placed on a watch glass. Use a side-to-side motion to evenly saturate the filter paper leaving a top portion dry in order to hang it.

23. Start the stopwatch and hang the saturated filter paper in the fume hood by the paper clip. After 20 minutes, weigh the filter paper.

24. Empty the 250 ml flasks into organic waste container.

25. Next day, weigh the dried thimbles and their content.

26. The difference in the initial and final weight of the dried filter paper is the bitumen recovered in grams in 5ml of bitumen+toluene solution. The total bitumen recovered from the froth sample is the total qty in 250 ml of bitumen+toluene solution.

27. The difference in the initial and final weight of the plastic bottles in which water is collected from the trap is the water in the froth.

28. The difference in the initial and final weight of the glass jar-containing thimble is the solids in the recovered froth.

APPENDIX C

This appendix contains results obtained for determining the correction factor for kerosene loss due to evaporation from the filter paper during bitumen recovery analysis in the Dean Stark analysis for correcting the net bitumen recovery.

C.1: KEROSENE LOSS DURING DRYING OF FILTER PAPER

The bitumen froth analysis for all the experiments carried out in this work is based upon using Dean Stark analysis procedure described in Appendix: B. As per the procedure, the amount of bitumen calculated in a particular experiment is determined by the difference of the weight of filter paper laden with bitumen (as a result of Dean Stark analysis) and the initial weight of dry filter paper. The dried bitumen-laden filter paper is a result of placing 5 ml toluene-bitumen solution obtained after recovering total quantity of bitumen from the bitumen froth sample using Dean Stark procedure. After applying 5ml of thoroughly mixed toluene-bitumen solution from the 250 ml volumetric flask, the filter paper is dried for 20 minutes. During these 20 minutes, all of the toluene evaporates from the filter paper leaving behind the bitumen present in the sample. The bitumen quantity that remains on the filter is used to calculate the total bitumen recovered in the froth.

Since, almost all of the experiments carried out in this work are based upon using naphtha or kerosene as a washing agent or for soaking in the ore, it has been assumed that the solvent thus used in the experiment becomes part of the froth recovered and is analyzed along with bitumen using Dean Stark method. Hence for all the results, the total quantity of solvent added in the ore was subtracted from the total bitumen recovered to represent the net bitumen recovery. Now since, naphtha and kerosene have higher volatility at room temperature as compared to bitumen, it was noticed that during Dean Stark analysis, some quantity of the kerosene or naphtha which become part of recovered bitumen froth and is mixed with bitumen-toluene solution evaporated during the 20 minutes drying of the toluene-bitumen filter paper. This loss of the solvent during drying of the filter paper was found to be the procedural loss of solvent during bitumen recovery estimation and contributed to errors in the results for net bitumen recovery.

C.2: EXPERIMENTAL PROCEDURE TO DETERMINE KEROSENE LOSS DURING DRYING OF FILTER PAPER

To estimate the error and calculate the adjustment factor required to take care of the loss of solvent used in the experiment during 20 minutes of drying of filter paper for determining net bitumen recovery of the experiment, separate experiments were carried out to determine the percentage loss of the solvent. The following procedure was used to determine the loss of kerosene due to drying of the filter paper:

- Experiments were carried out using 5 samples of 5 g each of bitumen (from Syncrude) and dissolving it into 200 ml of toluene. This solution was taken into five different distillation flasks of Dean Stark Apparatus. In the five respective distillation flasks 0 ml, 2ml, 4ml, 6ml and 15 ml of kerosene were added and Dean stark apparatus was arranged for distillation without any thimbles. (5 g of pure bitumen was used, considering about 4-6 g of bitumen recovery in actual experiments in one of the four thimbles used for collecting bitumen froth for 2, 3, 5 and 10 minutes of froth collection.)
- Heating of the distillation setup was carried out for two hours followed by 5-6 hours of cooling in line with standard Dean Stark procedure.
- After cooling of the apparatus, the kerosene mixed toluene-bitumen solution was transferred to respective 250 ml volumetric flasks. The solution in each volumetric flask was diluted with toluene to precisely fill the 250 ml volumetric

flask upto graduated marking and was thoroughly mixed by shaking the volumetric flasks.

- A pre weighed dry filter paper was weighed and placed on a watch glass. A 5 ml pipette was filled with the bitumen-toluene solution from each volumetric flask and dispersed on the respective filter paper uniformly.
- All the five filter papers were dried in the fume hood and the weight of all the filter papers were checked at the interval of 5 minutes for 60 minutes to determine the evaporation rate of toluene as well as kerosene from the filter paper during the drying step.
- Figure C.1 shows the residual Bitumen+Toluene+Kerosene on the filter papers for 5 cases in which 0 ml, 2ml, 4ml, 6 ml and 15 ml kerosene was added in 5 g of bitumen diluted in 250 ml of toluene. The residual hydrocarbons on the filter paper were noted at 5 minutes interval for the 60 minutes evaporation from the filter paper.
- It was noticed that for the base case where no kerosene was added, the weight of the filter paper stabilized after 15-20 minutes but for the cases in which kerosene was added in the bitumen-Toluene solution, the weight of filter paper kept on decreasing after 20 minutes and stabilized at later times for various levels of kerosene addition.
- This decrease in weight of filter paper for the cases in which kerosene was added in the Bitumen-Toluene solution represents that the kerosene in the solution when dispersed on the filter paper also evaporates along with toluene but at a very slow

rate. This is in contrast to the bitumen phase, which remains absorbed on the filter paper and does not evaporate.

- The data corresponding to 20 minutes of drying period has been detailed in Table C.1 for all the 5 cases to determine the loss of kerosene from the filter paper along with toluene in the fume hood. It is noted that corresponding to 20 minutes reading of the weight of filter paper, the loss of kerosene is on an average 10% for the cases in which kerosene was added as compared to the base case.
- Similar set of experiment was carried out using 20 g of bitumen dissolved in 200 ml of toluene and adding 0ml, 2ml, 4ml, 6ml and 15 ml kerosene in the bitumen toluene solution for Dean Stark analysis. The results of the same are shown in Figure C2 and Table C2. The loss of kerosene in this case was on an average 7.5% for the cases in which kerosene was added as compared to the base case.
- However for all the experimental work conducted in this work a correction factor of 10% has been used in increasing the bitumen recovery determined using Dean Stark analysis as all the data was taken corresponding to 20 minutes evaporation of toluene+solvent from the filter paper.

Hence, the net bitumen quantity in a froth used in any of the experimental result used for determining bitumen recovery is the result of 10% increase of the results obtained from Dean Stark analysis and subtracting from it the amount of solvent added

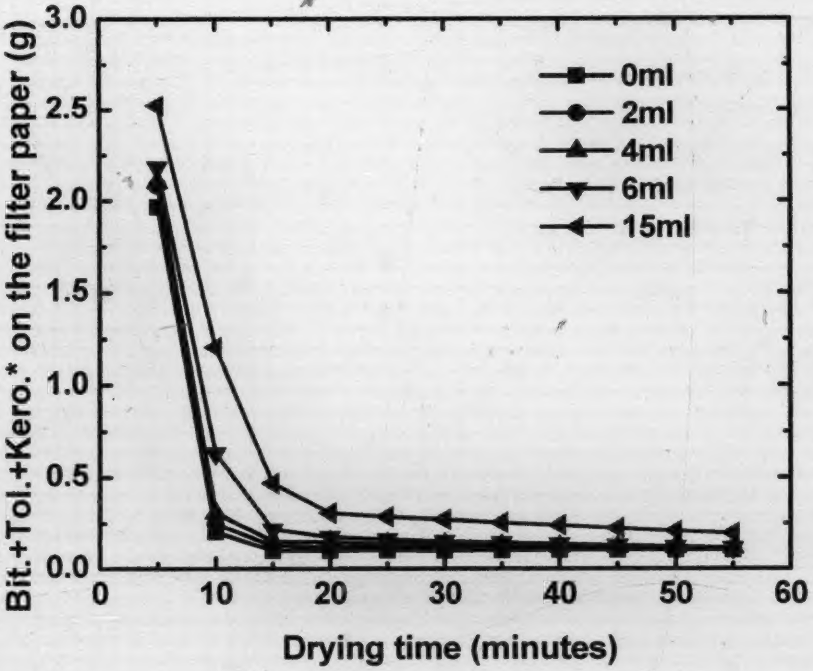
i.e. **Bitumen quantity in froth (g) =** $\frac{250}{5}$ *** (X) *1.1- Y**

Where

X = The amount of bitumen estimated using Dean Stark method for 5 ml Bitumen+Toluene solution placed on the filter paper

Y = Amount of solvent added in the ore (or on the bitumen froth) in grams

And factor 1.1 is a correction factor to account for the kerosene procedural loss during drying of filter paper

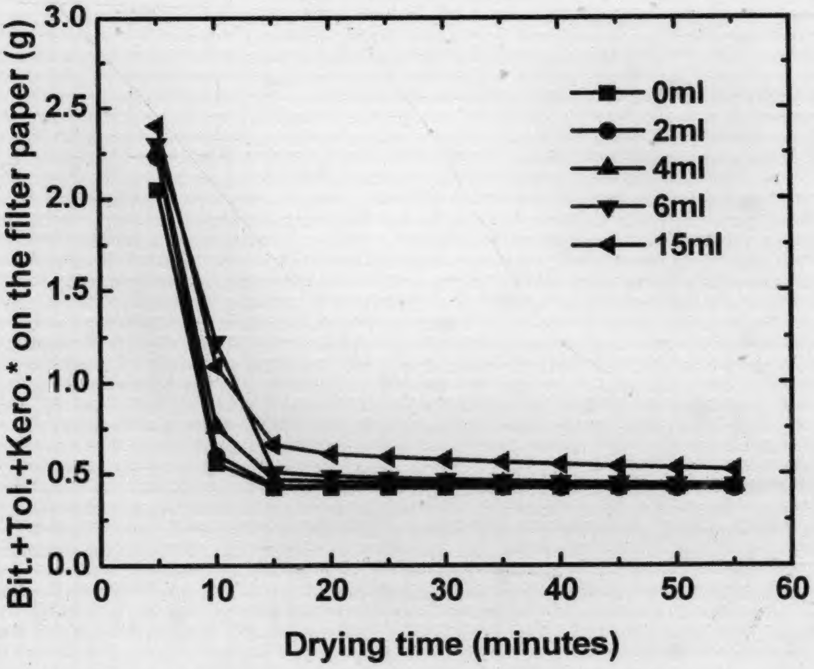


* Bitumen+Toluene+Kerosene on the filter paper during drying

Figure C.1: Toluene and kerosene evaporation rate from the filter paper to determine kerosene procedural loss for 5 g bitumen after 20 minutes of drying

Table C.1: Determination of kerosene procedural loss for 5 g bitumen sample in Dean Stark analysis after 20 minutes of drying

Kerosene added in 5 grams of bitumen + 200 ml of Toluene		**0 ml**	**2 ml**	**4 ml**	**6 ml**	**15 ml**
Bitumen used	g	5.0028	5.0028	5.0869	5.0946	5.0035
Kerosene added	ml	0.00	2.00	4.00	6.00	15.00
	g*	0.00	1.60	3.20	4.80	12.00
Total Kerosene+ Bitumen	g	5.00	6.60	8.29	9.89	17.00
Initial wt. of filter Paper	g	1.14	1.13	1.13	1.13	1.14
Final wt. of filter Paper	g	1.24	1.25	1.27	1.30	1.44
Bitumen in 5 ml Bitumen - Toluene solution	g	0.10	0.12	0.15	0.17	0.30
Bitumen in 250 ml Bitumen - Toluene solution	g	4.98	5.98	7.30	8.72	15.24
% Recovery Bitumen+Kerosene	**%**	**99.5**	**90.6**	**88.0**	**88.1**	**89.6**
Average % Recovery of Bitumen+Kerosene	**%**	**99.5**	**89.1**			
Loss of kerosene in 20 minutes of drying of filter paper (99.5-89.1)	**%**	**10.4**				



* Bitumen+toluene+kerosene on the filter paper during drying

Figure C.2: Toluene and kerosene evaporation rate from the filter paper to determine kerosene procedural loss for 20 g bitumen after 20 minutes of drying

Table C.2: Determination of kerosene procedural loss for 20 g bitumen sample in dean stark analysis after 20 minutes of drying

Kerosene added in 5 grams of bitumen + 200 ml of Toluene		**0 ml**	**2 ml**	**4 ml**	**6 ml**	**15 ml**
Bitumen used	g	20.012	20.093	20.055	20.086	20.049
Kerosene added	ml	0.00	2.00	4.00	6.00	15.00
	g*	0.00	1.60	3.20	4.80	12.00
Total Kerosene+ Bitumen	g	20.01	21.69	23.26	24.89	32.05
Initial wt. of filter Paper	g	1.13	1.14	1.14	1.14	1.14
Final wt. of filter Paper	g	1.55	1.57	1.59	1.62	1.75
Bitumen in 5 ml Bitumen - Toluene solution	g	0.42	0.43	0.46	0.49	0.61
Bitumen in 250 ml Bitumen - Toluene solution	g	20.62	21.15	22.41	23.82	29.74
% Recovery Bitumen+Kerosene	%	99.8	94.3	93.2	92.5	89.6
Average % Recovery of Bitumen+Kerosene	%	**99.8**	**92.4**			
Loss of kerosene in 20 minutes of drying of filter paper (99.8-92.4)	%	**7.4**				

APPENDIX D

This appendix consists of the results and discussion of the analysis of kerosene loss to the tailings water for 0 ml, 4 ml and 15 ml kerosene soaked in poor processing ore and extraction done at 50°C and 25°C, respectively. The results are based on carbon (C10-C20) area count in the tailings water estimated using Gas Chromatograms. The tailings water samples were generated in UofA laboratory and were analyzed by Maxxam Analytics, Edmonton.

D.1: BASIS FOR DETERMINATION OF KEROSENE LOSS INTO TAILINGS WATER

Kerosene is composed of carbon chains comprising C10-C20 carbon count and C/H wt. ratio of 0.49.The analysis of tailings water for determining the loss of kerosene added in the ore is based upon using gas chromatograms for the estimation of C10-C20 carbon count with respect to retention time in the tailings water samples and comparing it with the C10-C20 count in the base case in which no kerosene was added in the ore.

Two different sets of tailings water samples were generated, three each for 50°C and 25°C extraction respectively for the kerosene soaked in poor processing ore A for 5 minutes for following six cases:

EXTRACTION AT 50°C

1. Tailings water from 0 ml kerosene soaked ore (Sample D4)
2. Tailings water from 4 ml kerosene soaked ore (Sample D5)
3. Tailings water from 15 ml kerosene soaked ore (Sample D6)

EXTRACTION AT 25°C

4. Tailings water from 0 ml kerosene soaked ore (Sample D7)
5. Tailings water from 4 ml kerosene soaked ore (Sample D8)
6. Tailings water from 15 ml kerosene soaked ore (Sample D9)

The analysis is based upon the comparison of the chromatograms results for these six different tailings water samples with that of the chromatograms obtained for the pure kerosene, diesel and motor spirit. These chromatograms represent the C10-C20 carbon area count obtained for various samples and are used to calculate the C10-C20 concentration in mg/L. Figures D.1, D.2 and D.3 show the C10-C20 carbon area count obtained for pure kerosene, diesel and motor oil respectively. Figures D.4-D.9, respectively show the C10-C20 carbon area count estimated for the solids free tailings water generated from the extraction of kerosene soaked poor processing ore A, soaked for 5 minutes for above six cases respectively.

Figure D.1 is a GC for pure kerosene, which shows C10-C20 spike between 2.0-4.0 minutes of retention time. Figure D.2 is a GC for pure diesel, which shows C10-C20 spike between 2.4-6.4 minutes of retention time. Figure D.3 is a GC for pure motor oil, which shows C10-C20 spike between 6.0-10.4 minutes of retention time. Figure D.4-D.9 shows the C10-C20 area count spikes for respective cases. Following are the observations for the samples D.4-D.9 as a result of comparison of these chromatograms with those of D.1-D.3:

1. The kerosene GC fingerprint is absent in sample D.4 and D.7 i.e. no spike is observed between 2.0-4.0 minutes. This is acceptable as these were the base cases at 50°C and 25°C in which no kerosene was added to the ore.
2. The GC fingerprints present at the lower retention time for sample D.5, D.6, D.8 and D.9 are consistent with kerosene as these samples show C-10-C20 spike between 2-4 minutes.
3. The GC fingerprints present at the lower retention time may include diesel. This attribute can be discarded with the assumption that the presence of GC fingerprints is due to kerosene addition in the ore for these cases.
4. All samples show a mid range GC fingerprints consistent with motor oil. The same is observed for D.4 and D.7 case too.

5. To estimate the amount of kerosene present, the relative area count of the C10-C20 area in each sample was compared to that of each total chromatogram. These estimates are not intended to include only kerosene, but all the components that feature C10 to C20. However for this work, the C10-C20 estimated is assumed to be due to addition of kerosene in the ore only.

6. The following are the C10-C20 concentrations in mg/L estimated for the six samples (as reported by Maxxam Analytics.):

Table D.1: Carbon count C10-C20 concentrations in mg/L in the tailings water

Sample No.	**C10-C20 concentration in mg/L**
D4	3.7
D5	4.89
D6	40.69
D7	1.6
D8	3.06
D9	18.59

Based upon above estimate and using C/H wt. ratio of 0.49 in kerosene, estimate of kerosene loss into the tailings water has been calculated and explained in Section 4.5.

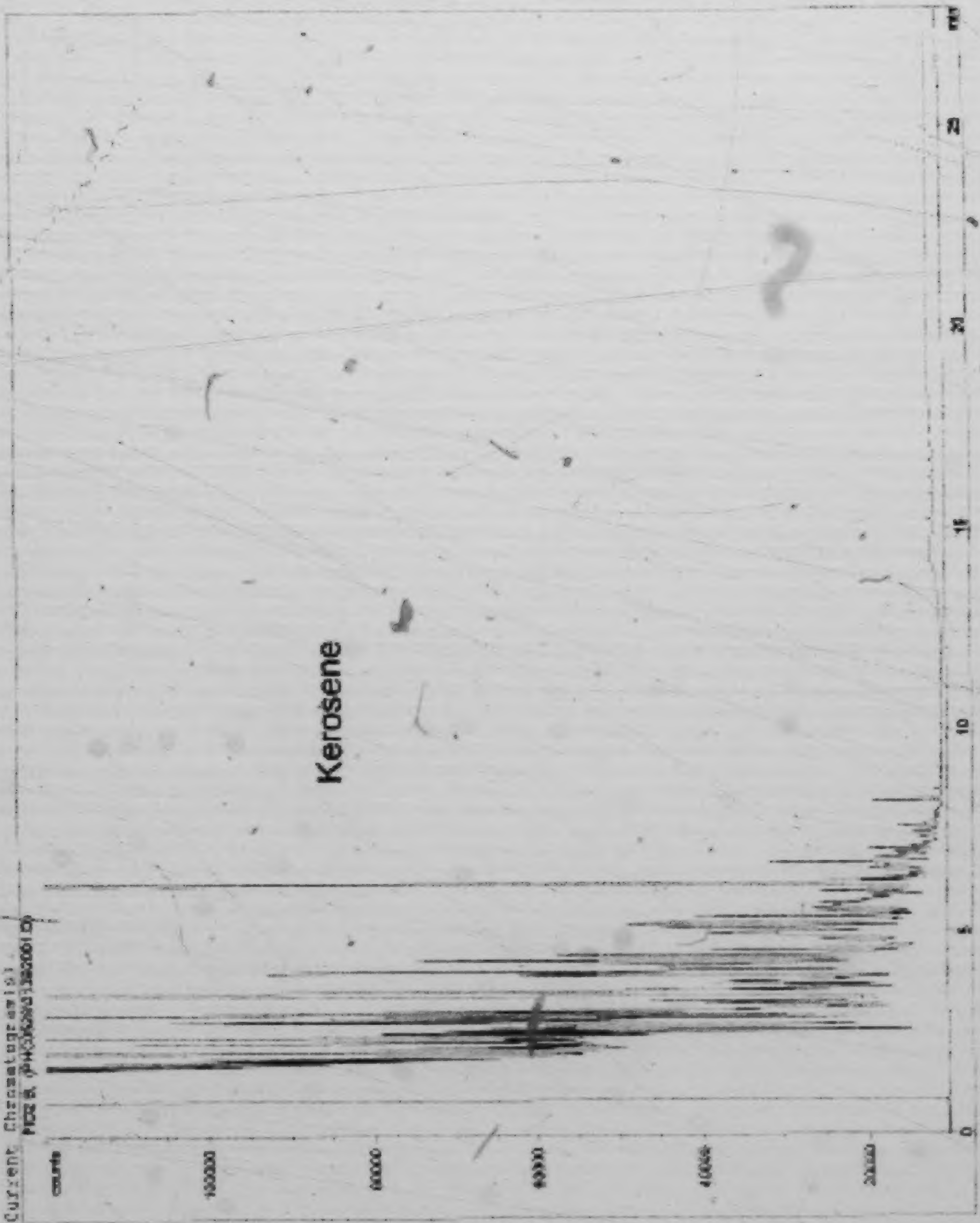


Figure D.1: Chromatogram of pure kerosene

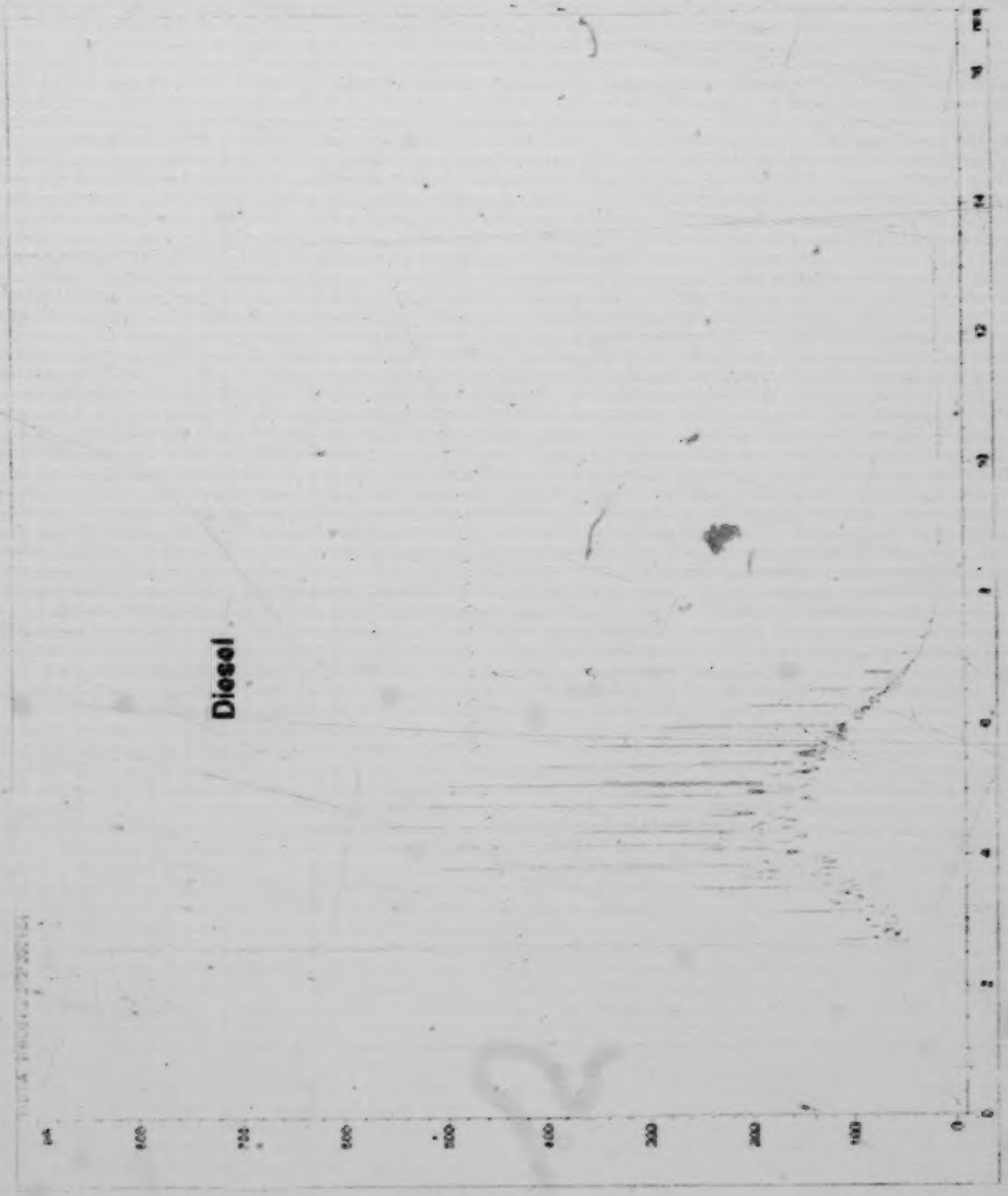


Figure D.2: Chromatogram of pure diesel

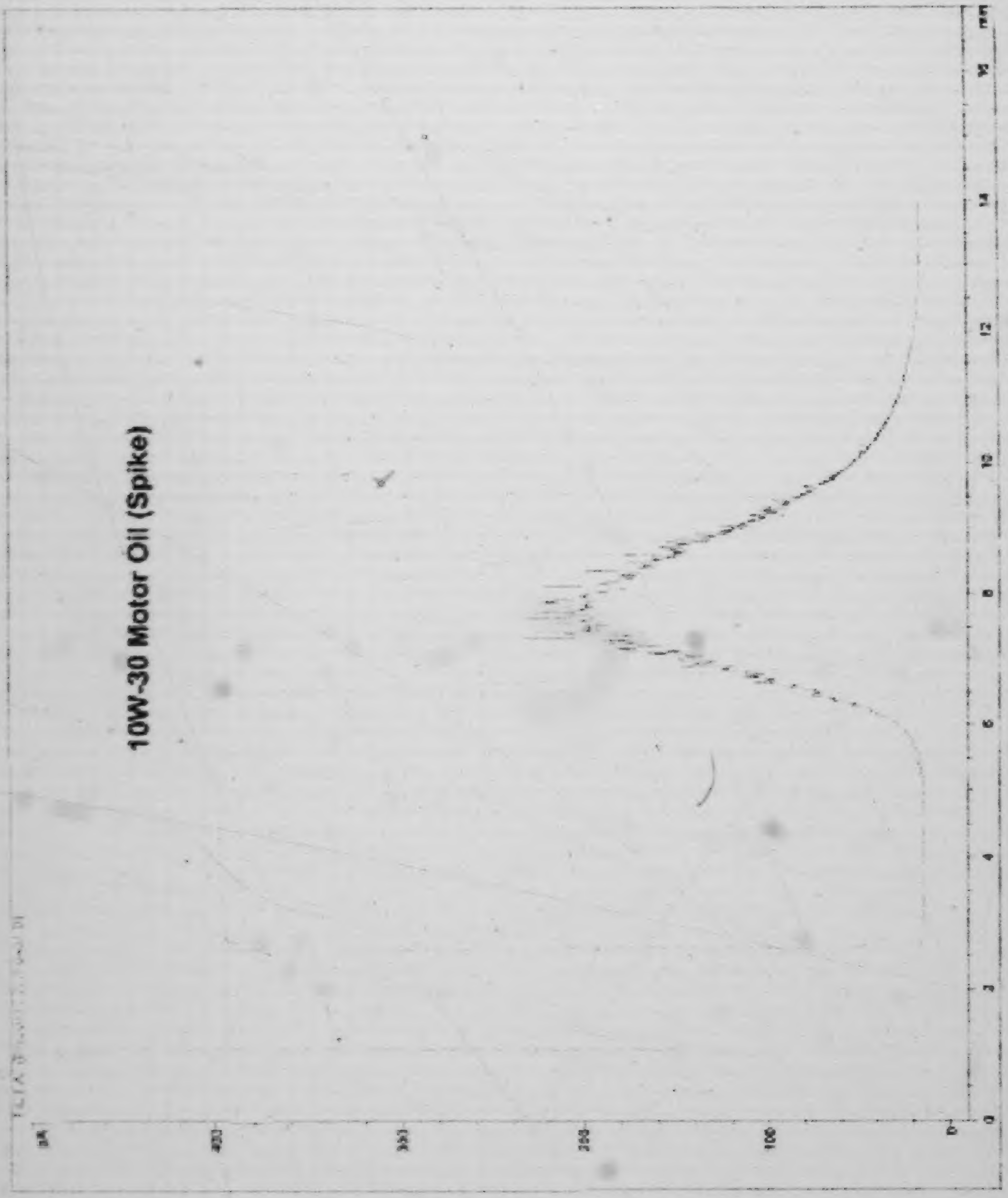


Figure D.3: Chromatogram of pure motor oil

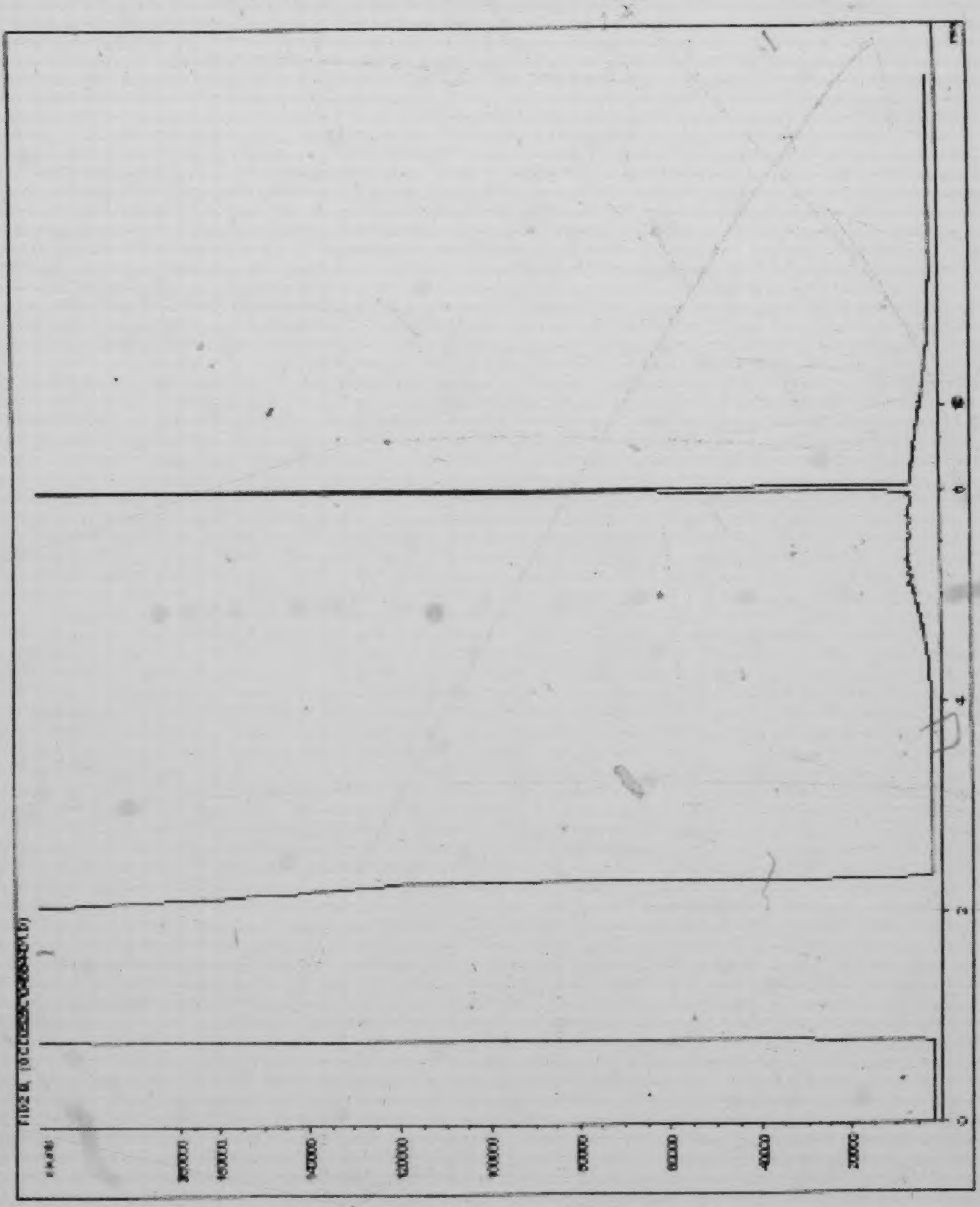


Figure D.4: Chromatogram of tailings water for 0 ml kerosene in poor processing ore at 50°C

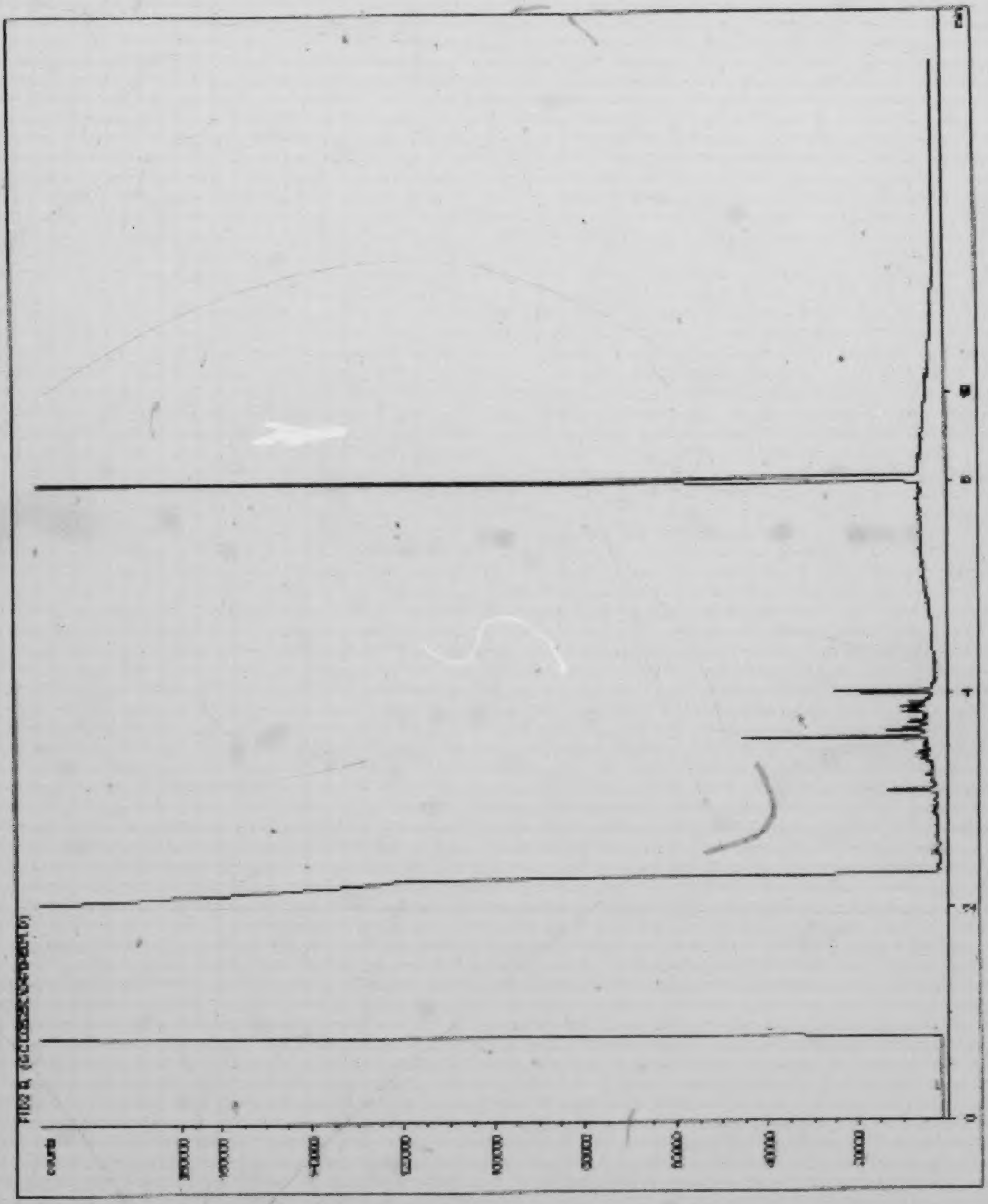


Figure D.5: Chromatogram of tailings water for 4 ml kerosene in poor processing ore at 50°C

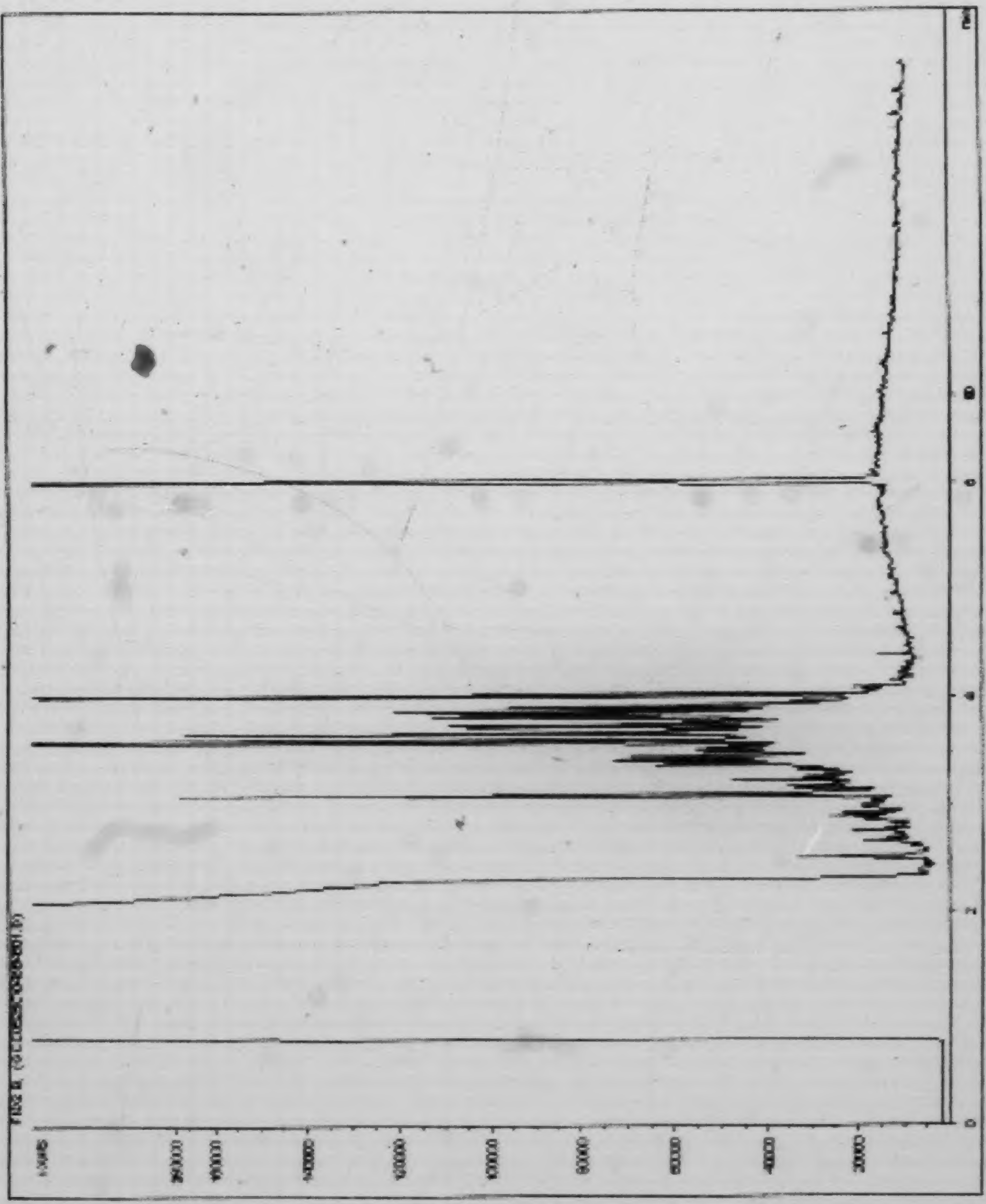


Figure D.6: Chromatogram of tailings water for 15 ml kerosene in poor processing ore at 50°C

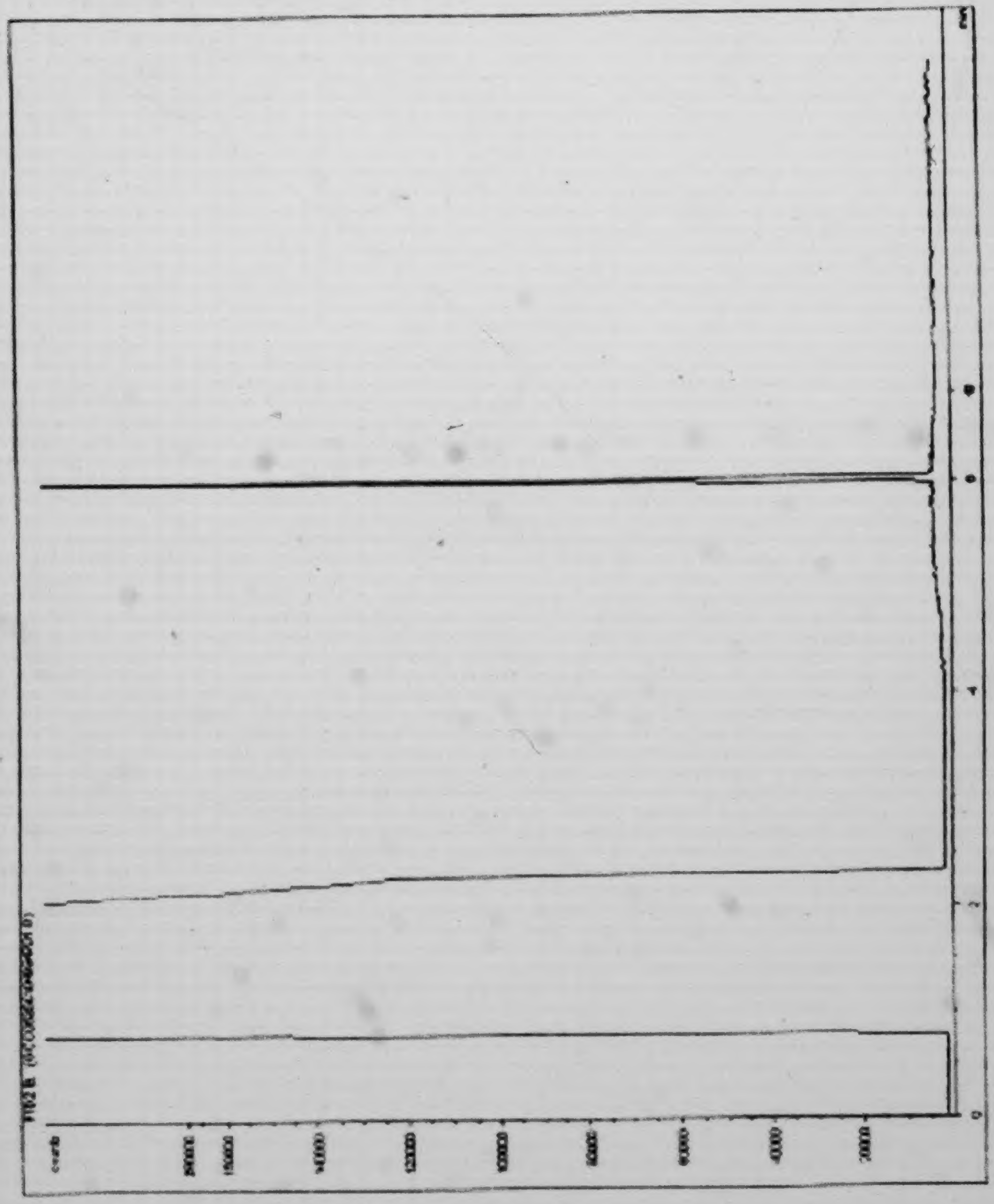


Figure D.7: Chromatogram of tailings water for 0 ml kerosene in poor processing ore at 25°C

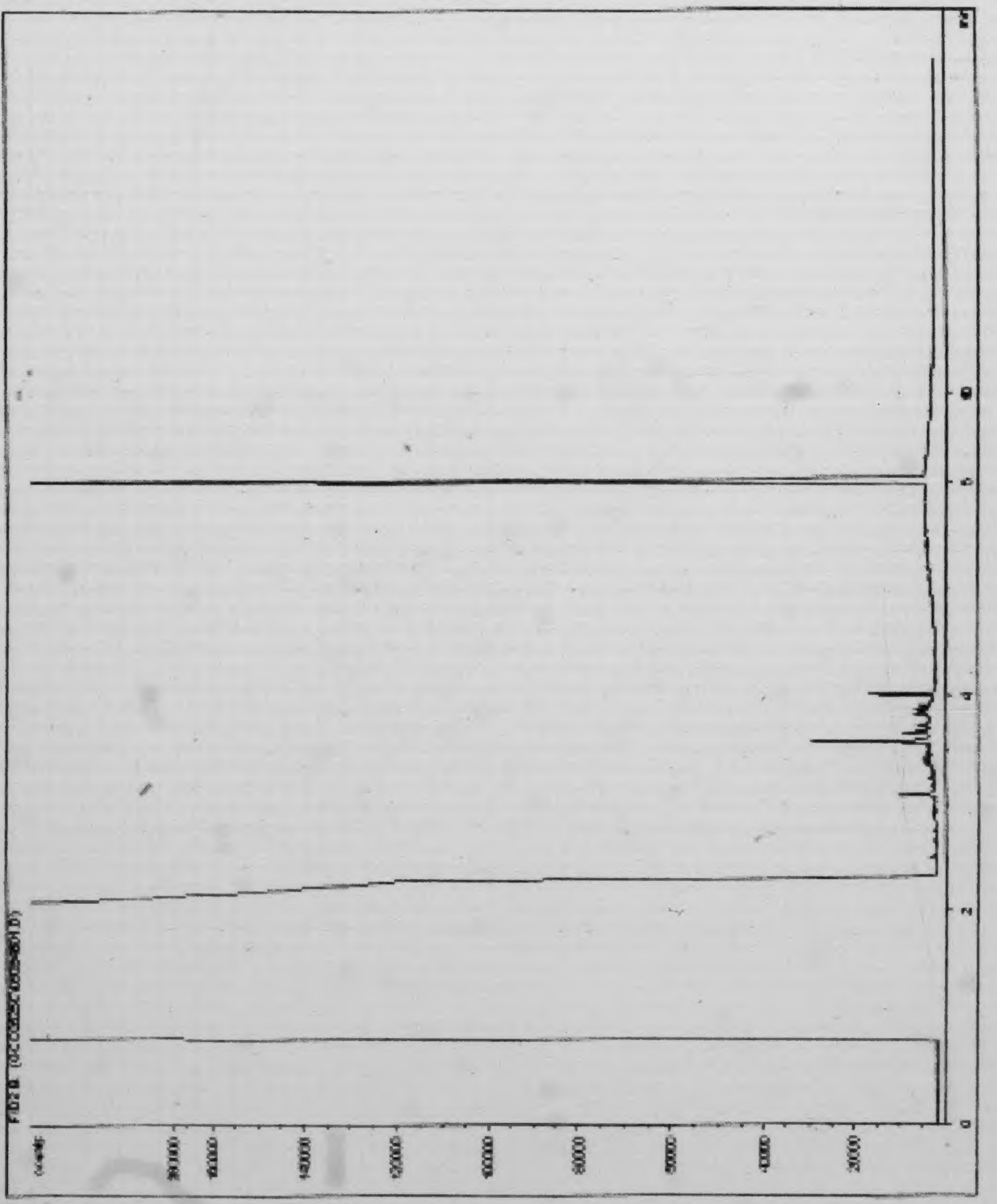


Figure D.8: Chromatogram of tailings water for 4 ml kerosene in poor processing ore at 25^oC

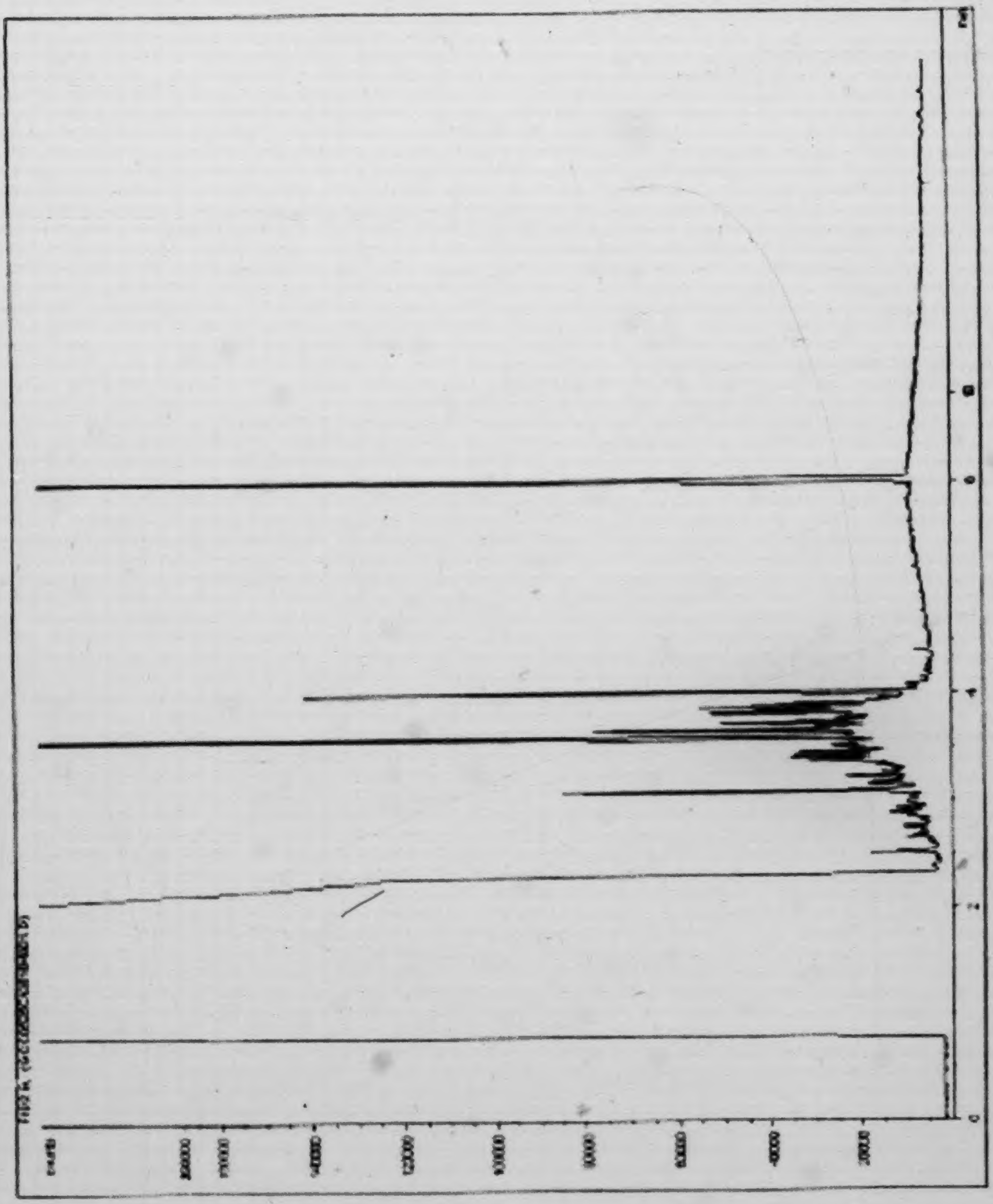


Figure D.9: Chromatogram of tailings water for 15 ml kerosene in poor processing ore at 25°C

APPENDIX E

This appendix consists of the results of experiments conducted to analyze zeta potential measurements for the fines from the solids recovered in the froth and the surface tension measurement of the tailings water for various cases.

E.1: ZETA POTENTIAL MEASUREMENT OF FINES IN THE SOLIDS RECOVERED WITH SOLVENT WASHED FROTH

Zeta potential measurements were carried out using a Zetaphormeter IV^{TM} (CAD) available in our laboratory. The Zetaphormeter is equipped with an electrophoresis chamber consisting of the electrode compartments and a connecting rectangular cell, a laser illuminator, and a digital video image capture and viewing system. By alternating the polarity of the electric field, the computerized operating system can capture the image of the moving particles, the stationary plane under a known electric field and then providing a histogram for electrophoretic mobilities of these particles using built-in image processing software. The data collected are converted to a zeta potential distribution. The instrument was operated at the room temperature and all measurements were performed using 1mM KCl solution in distilled water as the background electrolyte. Each test was repeated for 6-8 times and the average results have been reported. The measurement error was generally less than 5%.

Zeta potential of the fines in the solids in the froth from good processing ore, poor processing ore and weathered poor processing ore soaked in 0ml, 2ml, 4ml, 6ml and 15 ml kerosene, respectively for 15 minutes and extraction done at 25°C for 20 minutes froth recovery was analyzed and the results for the same are shown in Figure E.1. No variation in the zeta potential for the fines in these cases was observed.

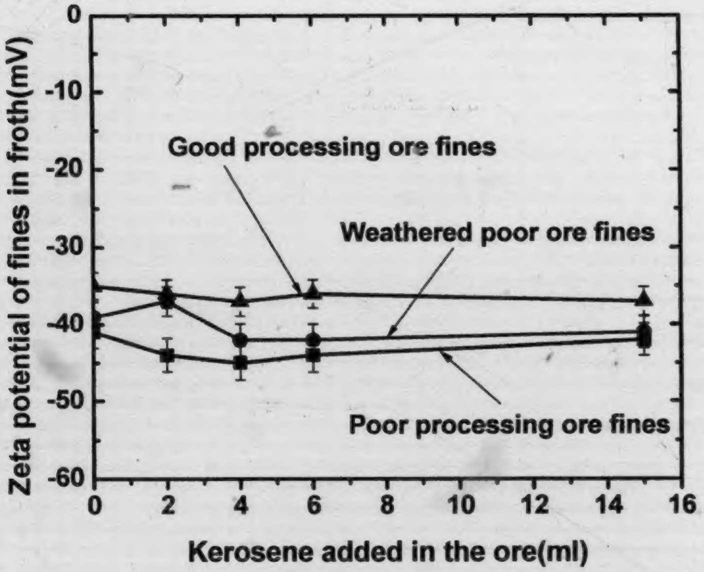


Figure E.1: Zeta potential of the fines in the solids in the recovered froth from different oil sand ores soaked in kerosene for 15 minutes and extraction done at 25°C for 20 minutes froth recovery

Another set of experiments was carried out to observe the zeta potential of the fines in the solids in the froth from poor processing ore soaked in 0ml, 2ml, 4ml, 6ml and 15 ml kerosene, respectively for 15 minutes and extraction conducted at 25°C and 50°C for 20 minutes froth recovery. All measurements were carried out at room temperature. As observed in Figure E.1, Figure E.2 also shows that no variation in the zeta potential for the fines in these cases.

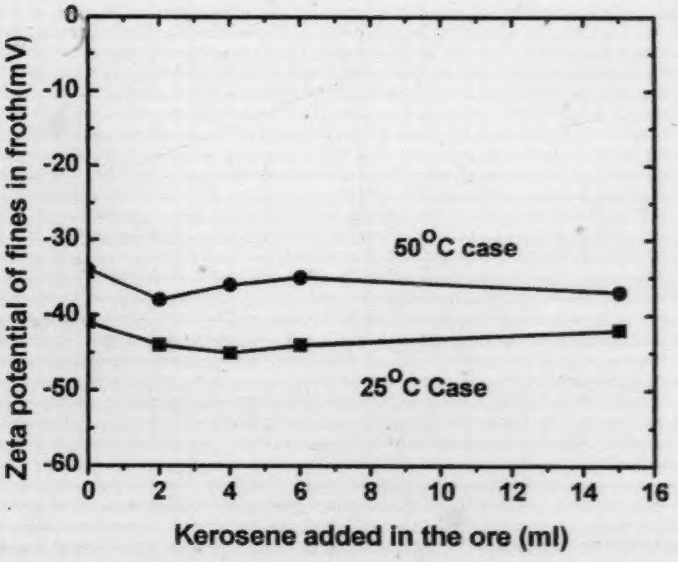


Figure E.2: Zeta potential of the fines in the solids in the recovered froth from poor processing ore soaked in kerosene for 15 minutes, extraction done at 25°C and 50°C for 20 minutes froth recovery

E.2: SURFACE TENSION MEASUREMENTS OF TAILINGS WATER

Another set of experiments was carried to observe the variation in surface tension of the tailings water due to addition of kerosene in the ore for soaking. The solids free tailings water for good processing ore, poor processing ore and weathered poor processing ore for 0 ml, 4ml and 15 ml kerosene addition in the ore cases and extraction done at 25°C were analyzed for surface tension using Tensiometer available in our laboratory. Figure E.3 shows the results obtained for the three cases. No variation in the surface tension of the tailings water was observed for the respective cases.

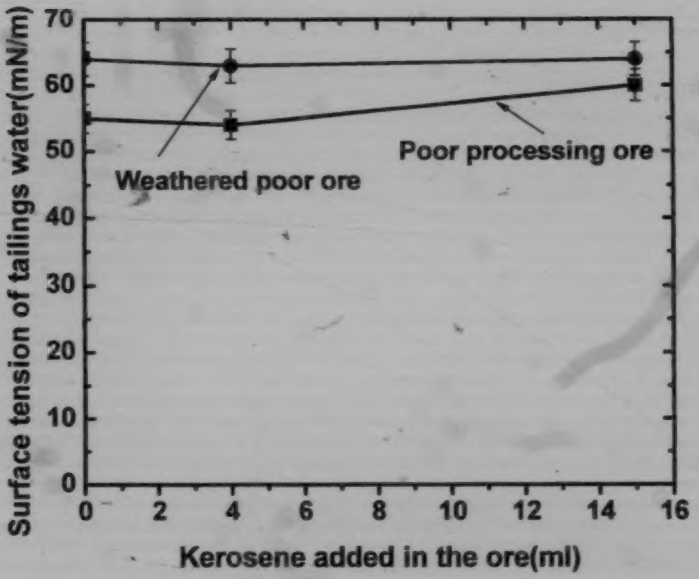


Figure E.3: Surface tension of the tailings water from different oil sand ores soaked in kerosene for 15 minutes and extraction done at 25°C for 20 minutes froth recovery